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The Determination of Lead in Lead Ores. By Richard K. Meade.

Note on the Separation of Silicic and Tungstic Acids. By James S. de Benneville.

Method of Drying Sensitive Organic Substances. By C. C. Parsons.

Determination of Silica in Blast Furnace Slag. By G. H. Meeker.

A New Form of Condenser for the Distillation of Liquids having Low Boiling Points. By Ervin E. Ewell.

Manufacture of Phosphor Bronze. By Max H. Wickhorst.

Analysis of Phosphor Bronze, Phosphor Copper, Phosphor Tin, etc. By Max Wickhorst.

The Normal Urine. By Charles Platt.

Theo. G. Wormley

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THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

PROF. THEODORE GEORGE WORMLEY.

BY EDGAR F. SMITH.

Received March 1, 1897.

ONE by one the men who contributed so materially in developing the science of chemistry in America are passing from among us. They have, for the most part, been men of broad training, who quietly, unostentatiously, but persistently, pursued some special line or branch of the science, and as a result of their untiring efforts have wrung from nature facts which possess not only a theoretical, but also practical value. In this band of earnest investigators and seekers after truth, none will deny a high position to him, whose name heads these lines.

As a member, councilor, and past vice-president of our Society his record may well claim our attention, while we pause to briefly note the lesson of his life and his achievements.

Little is known of the early days of Professor Wormley, other than that he was born in 1826 at Wormleysburg, one of the numerous villages nestling among the hills of that garden-spot of Pennsylvania—Cumberland County—the birthplace of so many men who have been powerful in affairs of the state and nation, as well as leaders in the various departments of learning.

His ancestors were Germans, who emigrated to America, as nearly as can be ascertained, about the year 1753. At what age the future professor left his native village for Carlisle, the seat of Dickinson College, remains unrecorded, but the records of that institution show that when sixteen years old (1842) he entered the preparatory department, where he

remained two years, when he was admitted to the Freshman class and continued in the regular course of study to the close of the Sophomore year. His name appears in the register of the College in the following year, but with the statement that he was pursuing a partial course.

Professor Wormley's vacations in these preparatory years were usually spent in scientific expeditions to the Western and Northern sections of the great state of Pennsylvania in pursuit of natural history studies. The leading spirit and guiding mind of these excursions was the late head of the Smithsonian Institution—Spencer F. Baird—then the curator of the museum and professor of Natural History in Dickinson College, "whose enthusiastic and unreserved devotion to science was calculated to awaken a deep interest in such studies * * * and a number of young men, who afterward achieved eminence, received their first impulse from him." Of this number was Theodore Wormley, whose predilection for science studies was also encouraged, promoted, and greatly influenced by another Dickinson professor, Dr. William H. Allen, then professor of chemistry in the college, but subsequently the presiding head of Girard College.

This early preference for scientific investigation, no doubt, led Professor Wormley to choose medicine as his profession, so that after the customary year of preliminary reading under the preceptorship of Dr. John J. Myers, we find him matriculated in the Philadelphia College of Medicine, an institution not existing at present, but from which he graduated in 1849. Then followed a year's residence in Carlisle, after which he removed to Chillicothe, O., remaining there but a short time, when he proceeded to Columbus, O., where the practice of his profession was begun. His first professional appointment came in the year 1852, when he was elected to the Chair of Chemistry and Natural Science in The Capitol University, located in Columbus, O. This position he held until July, 1865. While holding this Chair he also held the professorship of Chemistry and Toxicology in Starling Medical College, to which he had been elected in 1854, and from which he resigned after twenty-three years of most satisfactory work. The hours not devoted to teaching or research were occupied in the discharge of appointments, for

which his qualifications admirably fitted him, such as State Gas Commissioner of Ohio (1867–1875), and Chemist of the Geological Survey of Ohio (1869–1874). In both these positions Professor Wormley rendered most distinguished service, as is amply evidenced by the various State Reports in which his records are published.

His acknowledged reputation among medical men as a teacher and toxicologist led to his election, on June 5th, 1877, to the Chair of Chemistry and Toxicology in the Medical Department of the University of Pennsylvania, becoming thereby the direct and worthy successor of such eminent men as Benjamin Rush, James Hutchinson, James Woodhouse, J. Redman Coxe, Robert Hare, and Robert E. Rogers. And here he continued until the morning of January 3rd, 1897, when the final summons came, and the earnest, ever-active master laid aside the working tools of life to penetrate the veil which separates us and the present from the great hereafter.

For forty-five years Professor Wormley taught and investigated. The results of his researches appeared under the following titles:

1. On Some of the Chemical Reactions of Strychnia. Chem. News, 1860.

2. Notes on Some of the Chemical Reactions of Atropine. Chem. News, 1860.

3. Notes on Some of the Chemical Reactions of Brucine. Chem. News, 1860.

4. Chemical Reactions of Corrosive Sublimate. Chem. News, 1860.

5. Chemical Reactions of Morphia. Chem. News, 1860.

6. Chemical Reactions of Narcotine and Meconic Acid. Chem. News, 1860.

7. Nobert's Test Plate and the Striae of Diatoms. Chem. News, 1861.

8. Quantitative Estimation of Urea. Chem. News, 1882.

9. Recovery of Absorbed Morphine from Blood. Chem. News, 1891.

10. A Contribution to Our Knowledge of the Chemical Composition of Gelsemium. Am. J. Pharm., 1870.

11. Alkaloids of Veratrum Viride and Alum. Am. J. Pharm., 1876.

12. Preparation and Toxic Effects of Gelsemia. Am. J. Pharm., 1877.

13. Reinsch's Test Fallacies. Am. J. Pharm., 1880.

14. Constitution of Gelsemium. Am. J. Pharm., 1882.

15. Some of the Chemical Properties of Mydriatic Alkaloids. Am. J. Pharm., 1894.

16. Tests for Quinine. Am. J. Pharm., 1894.

17. Recovery of Absorbed Morphine from the Urine, the Blood, and the Tissues. Univ. Med. Mag., 1889-90.

18. Concordant and Micrometric Measurements. Univ. Med. Mag., 1890–91.

19. Chemical Analysis of Coals, Iron Ores, etc. Ohio Geol. Survey, 1870.

Editor of the Ohio Medical and Surgical Journal, 1862–1864.

These in a measure indicate the direction of his activity, but the lasting monument which he raised to science and his own glory is his grand work entitled "Micro-Chemistry of Poisons." In it are embodied the records of thousands of the most painstaking observations. The patience displayed in the preparation of this volume of world-wide reputation — the recognized authority in all lands—is marvellous. It is interesting also to note that in this, his greatest effort, he was assisted by his devoted wife, who learned the art of steel engraving solely for the purpose of delineating upon steel nearly one hundred exquisite illustrations of crystals, drawn directly from the object as observed under the microscope.

A marked characteristic of all work done by Professor Wormley is its extreme accuracy. In searching for the truth, time and labor ceased with him to be factors. Repetition was practiced to an almost painful degree. Every subject was studied from all possible points of view, so that in his special field it is not in the least surprising that he was early recognized as an authority and expert.

As a teacher he ever maintained a high rank. His power of imparting knowledge was equaled by few. That patient spirit which dominated all his work manifested itself here and is evidenced by thousands of students to-day. Details were presented with care, and every effort was made to have even the dullest neophyte understand. It was ever the aim of the professor to have the principles of the science thoroughly grasped and comprehended by his pupils. Superficiality he despised. Thoroughly conversant with his subject, he possessed the power of presenting it in an extremely lucid manner.

Though modest and retiring to a degree, Professor Wormley was the recipient of many honors, and received elections to many scientific societies. Thus he was one of the Vice-Presidents of the Centennial of Chemistry, held in Northumberland, Pa., in 1874; a member and Vice-President of the American Chemical Society; a member of the American Philosophical Society; a member of

the American Metrological Society; a corresponding member of the New York Medico-Legal Society; a Fellow of the College of Physicians, Philadelphia; a Fellow of the American Association for the Advancement of Science, and a Fellow of the Chemical Society of London.

In 1870 he received the honorary degree of Doctor of Philosophy from Dickinson College, and the same degree from Pennsylvania College in 1877, while Marietta College, Ohio, conferred upon him the degree of Doctor of Laws in 1870.

Personally Professor Wormley was a modest, unassuming man. Few knew him well. Those who were fortunate enough to brush aside the mantle of reserve which usually surrounded him, found a genial, kind, sympathetic companion, with a mind stored with the most varied knowledge and ready to unfold itself to those who had won his confidence. In his comments upon the work and writings of others he was extremely considerate. No bitter criticism was ever allowed to pass his lips, no matter how widely the views set forth by their authors may have differed from what he believed to be correct. True, upright and just in his dealings with all men, it is not surprising that he won the hearts of the great student body and of all with whom he came in contact. By them his memory will ever be cherished as one who loved and sought the truth alone, who was content in the quiet of his laboratory, away from the noise and bustle of the world, to work out the facts, which as we find them arrayed in his great work, will cause future students of chemistry to render to his name that homage which ever falls to the master in any great effort.

NOTES ON CAFFEIN.

By G. L. Spencer.

Received January 13, 1897.

SHORTLY after submitting the above title to the Secretary, the November, 1896, number of the Journal was received, which included a paper on the estimation of caffein. This paper in many respects anticipated the notes I intended submitting to the Society.

It was my intention to discuss some of the statements of Gomberg[1] in his paper describing his volumetric method for caffein,

[1] This Journal, 18, 331.

using Wagner's reagent. Gomberg cites certain experiments in which he secured but a small proportion of caffein present in a certain sulphuric acid solution of the alkaloid, even after shaking many times with chloroform. The experience of Allen,[1] or Puckner,[2] and my own work all demonstrate that the caffein may practically be entirely removed from water solution by shaking four or five times with chloroform. However in a number of instances I detected a trace of caffein by the "murexid test," and in later work by Wagner's reagent, as recommended by Gomberg, in the watery residue, left after five extractions with chloroform. In view of this fact and the frequent necessity of slight acidulation of the solutions with sulphuric acid to reduce the tendency to the formation of obstinate emulsions, the writer deemed it advisable, for precautionary reasons, to recommend seven extractions, in the publication of the gravimetric method[3] from which Gomberg quotes in his paper Unless great care is observed in the gravimetric method in the recovery of the chloroform by distillation, an error may result from the entrainment of caffein with the chloroform vapors. A safety bulb, such as is made for use in the Kjeldahl nitrogen process, effectively prevents loss of caffein in the distillation.

It is difficult in the gravimetric method to obtain an absolutely pure caffein, there being usually sufficient foreign matter present to give a slight coloration in the cold with concentrated sulphuric acid. This contamination with foreign matter is probably too slight to appreciably affect the accuracy of the results. The two methods give almost identical results as shown by the following examples. The same purified solution was used for each of the methods:

Description of samples.	Gravimetric method.	Gomberg's method.
1. Mixed tea	2.24	2.21
2. Japan tea dust	2.27	2.28
3. Japan tea dust	2.29	2.30

The following method of purifying the caffein was tried with Sample No. 3 with a promising degree of success: Five grams of the finely ground tea were boiled thirty minutes with approximately 400 cc. water; a considerable excess of recently prepared

[1] Commercial Organic Analysis, 3, Part II, 485.
[2] This Journal, 18, 978.
[3] *J. Anal. Chem.*, 4, 390.

ferric hydroxide was added, and after digesting about one hour, the mixture was cooled and transferred to a graduated flask and diluted to 500 cc. An aliquot part of the solution was filtered off and treated by Gomberg's method. The difficulty experienced was in filtering off the periodide of caffein. The percentage of caffein obtained was 2.28, as compared with 2.29 and 2.30 by the other methods. The solution of caffein obtained by this method is not sufficiently pure for the extraction of the alkaloid by chloroform for analytical purposes.

In comparative experiments with a number of methods for the determination of caffein in teas, the Gomberg method has given the most satisfactory results and admits of wider application than the gravimetric methods.

SOME APPARATUS FOR THE TECHNICAL ANALYTICAL LABORATORY.

By Edward S. Johnson.

Received February 1, 1897.

THOSE branches of chemical industry which are dependent in part for guidance upon an analytical laboratory are each year becoming more exacting in regard to their demands upon the laboratory for accurate, yet rapid, work in large quantity.

Besides stimulating research with a view to shortening established methods of analysis, or the invention of new ones requiring less time for their execution, this exaction has resulted further in the introduction of much special apparatus for expediting the routine operations of the laboratory. A visit to any of the well-conducted technical laboratories of the day will show that much work of this sort has been done, and the frequent contributions on the subject in the contemporaneous journals of chemistry give evidence that activity in this direction is not abating.

It is the purpose of the present communication to present a few forms of apparatus designed in the first instance to facilitate and hasten the work of the technical laboratory with which the writer is connected. The efficient service which these devices have rendered induces him to venture upon their description with the thought that it may prove of interest to others engaged in the same field of work—the analysis of iron and steel. Although more particularly adapted to the special work mentioned, the ap-

paratus, in some cases, may perhaps be found capable of advantageous application in connection with other branches of technical analysis, and possibly, in one or two instances, in the general analytical laboratory. In its application it concerns the operations of: I. Measuring Reagents; II. Filtration; III. Solution with the Aid of Heat.

I. MEASURING REAGENTS.

As is well known, the technical analyst is constantly required to treat a large number of samples or solutions successively with a given quantity of some liquid reagent in order to obtain a solution, effect a precipitation, etc., *where great accuracy is not important.* Such manipulations may be speedily executed by the simple arrangement shown in Fig. 1.

A reservoir of several liters capacity, containing the reagent, is connected by a siphon with a measure, and the whole mounted upon a stand with castors. The stand *S* is of finished oak, and ten to eleven inches in height. In its top there is a shallow circular space slightly larger in diameter than the reservoir *R* which, in this case, is a four-liter bottle. This sufficiently secures the reservoir in its position on the stand. The bottle is closed by a rubber stopper into which two glass tubes are inserted, *T* reaching to the lower surface of the stopper, and *M*, of one-quarter-inch tubing, which extends to the bottom of *R* and forms the siphon connecting with the graduate. The latter is provided at both ends with accurately ground stop-cocks. At *V* is a vent through which air escapes or enters as the graduate is filled or emptied. In the upper end of the measure and directly under the opening in the stop-cock, a short piece of tubing is fused. It directs the liquid as it enters the measure, preventing its running down the walls and consequent escape at *V*. A clamp attached to a stout wooden peg fixed in the under side of the top of the stand holds the graduate firmly.

Until the supply of reagent in the reservoir is exhausted, the apparatus is clearly ready for continuous service after the filling of the siphon. This, plainly, may be done either by applying pressure through *T* or suction at *V*, the lower stop-cock being first closed. When used it is drawn to the edge of the work-table, where the graduate projects slightly, and the reagent may be conveniently delivered into the vessels destined to receive it.

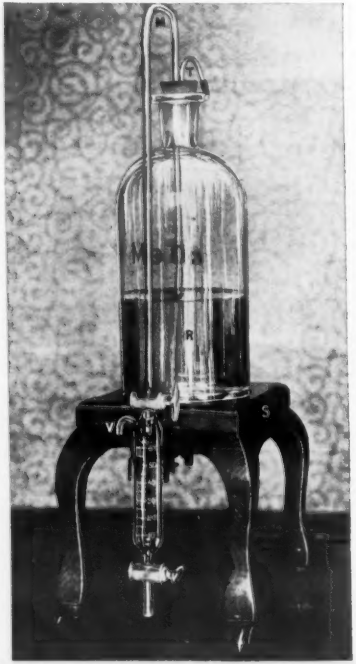

Fig. 1.

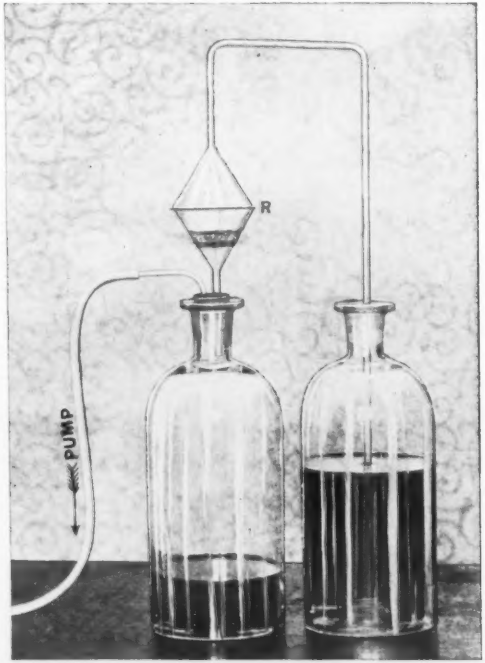

Fig. 2.

Fig. 3.

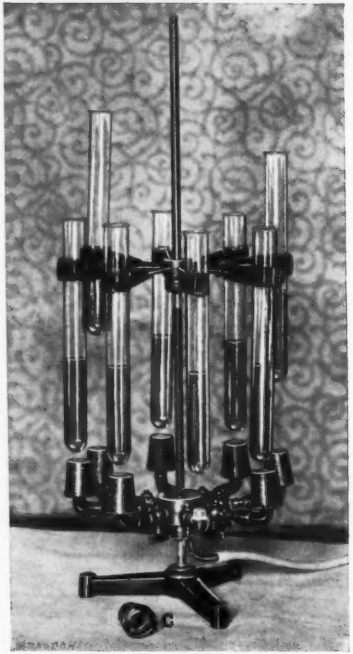

Fig. 4.

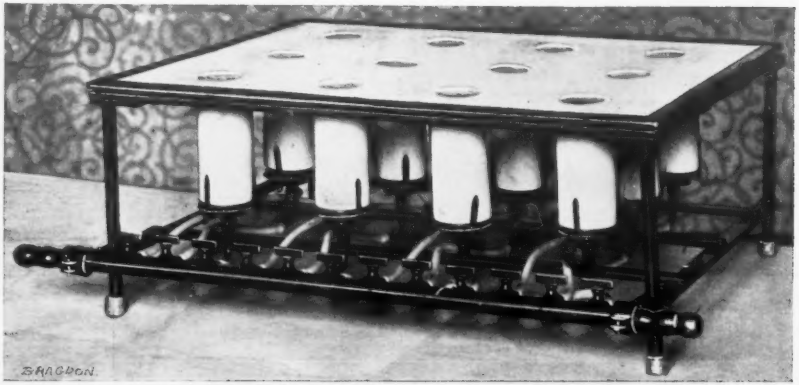

Fig. 5.

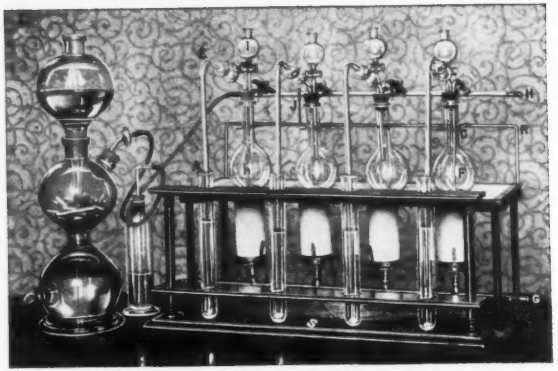

Fig. 6.

As the level of the liquid in the reservoir falls, the rapidity of the flow from the siphon of course decreases. Should the delivery become too slow, a force-pump (rubber bulb with valve) may be used to restore the failing pressure. When this addition is made, it is convenient to attach a piece of rubber tubing with a pinch-cock at *T*. It allows of quickly relieving the pressure within the reservoir. A third tube bent like *T*, but having a small bulb in the outer shank, connects with the pump. The bulb is filled with cotton which filters the air forced through the tube. Where reagents contain solids in solution, it is usually necessary, to avoid the sticking of the stop-cocks, to clean them and the graduate directly after using, especially when some time must elapse before the apparatus is again used.

In some analytical work, it is desirable to be able to deliver larger volumes (200 to 250 cc.) than is possible with the arrangement just described. This, however, is easily adapted to the work indicated. The height of the stand remains the same. The reservoir has the same capacity, or may be larger, according to the demand made upon its contents. *M* may be of somewhat larger diameter with advantage; it no longer acts as a siphon, and merely connects reservoir and measure. The measure with its increased capacity is much longer than before, and is so placed that the outer end of *M* is above the level of the liquid in the filled reservoir. The upper stop-cock may then be dispensed with, as the graduate is filled by means of the force-pump and the flow of the reagent from *M* may be instantly stopped by opening the valve (rubber tubing with pinch-cock) which is added at *T*. This and the pump, conveniences in the form of the apparatus seen in the figure, now become necessities.

By substituting for the graduate a burette, an extremely practical combination is obtained for *measuring small volumes accurately*. *M* must be made higher and dips about one inch into the burette without being attached to it. A disk of soft rubber with a hole to allow the passage of the tube, closely covers the mouth of the burette. Further, a second clamp is needed to retain the burette in a vertical position. It grasps the neck of the bottle at one end and the burette at the other, and is a simple adaptation of a familiar form of clamp. The filling of the bu-

rette, as need hardly be remarked, is conducted exactly as described for the arrangement with the larger measure.

This modification of Fig. 1 was devised for use in connection with the colorimetric determination of carbon in steel. It has so effectually aided in the work that it now seems almost indispensable. It is necessary for obvious reasons to do the work referred to in the draft-chamber. When not in use, the appliance must be kept out of the way of other apparatus and work, usually back against the wall of the chamber out of easy reach for service. The facility with which it may be moved to a convenient position when needed becomes here an especial advantage.

II. FILTRATION.

1. *Filtering Apparatus with Automatic Feed.*—For certain phases of the routine work of the technical laboratory, the necessary reagents require preparation in large quantities as an economy of time. This involves, as a rule, the filtration of solutions several liters in volume. With the device seen in Fig. 2, readily constructed from materials always at hand in the laboratory, such filtrations are rapidly executed with extreme convenience. Of the two bottles shown in the cut, the one on the right contains the unfiltered solution, while the other receives the filtrate and carries the filter noticed in the funnel held by the rubber stopper in the neck of the bottle. The filter is of thick felt formed from paper or asbestos pulp upon a perforated porcelain filtering-plate.[1] The funnel is about four inches in diameter and has a carefully ground edge. For most purposes, a plate one and a half to two inches in diameter will answer. Resting on the funnel with the filter is a second inverted one of the same diameter, also having a ground edge, and with a long stem bent to reach to the bottom of the bottle containing the solution to be filtered. A ring of soft rubber *R*, between the funnels, and their ground edges effectually secure an air-tight joint when external pressure is applied. It was first intended to use funnels with quarter-inch flanges as a means of fitting them together. The

[1] O. N. Witt: *Ber. d. chem. Ges., 1886*, 918. This exceedingly useful form of filter in the preparative work of the laboratory, particularly the organic laboratory, whether it be desired to clear a solution or collect a precipitate, has recently been used in my laboratory with advantage in certain *quantitative work*. By means of the pulp-filter, tungstic hydroxide, for instance, a most troublesome precipitate to handle in large quantities, may be collected and washed with little difficulty.

above simpler arrangement, however, as intimated, works perfectly. The end of the stem of the upper funnel has a lateral opening,[1] obviously that the solution may have unhindered entrance.

The preparation of the filter (making the pulps and forming the felt upon the plate) needs no explanation. When asbestos is used it should first be ignited. The fibers then become somewhat elastic and produce a spongy, rapid filter. The felts are usually three-eighths to one inch thick, according to the difficulty of the filtration, the thicker felts being used for the more obstinate cases.

The filtration is begun, after placing the parts of the apparatus as seen in the figure, by starting the filter-pump. The bottle to receive the filtrate and the space enclosed by the funnels, as a result, are partially exhausted of air. The external air-pressure now being considerably greater, the funnels are pressed forcibly together. The solution to be filtered rises and flows upon the filter, the flow continuing only as fast as liquid is withdrawn; the solution is thus automatically fed to the filter. The apparatus requires no further attention until the filtration is complete.

2. *A Revolving Filter-Stand.*—This device is represented by Fig. 3. The tripod base carries a vertical steel rod about three-eighths of an inch in diameter and eight inches high. Its free end is rounded and forms the pivot for the rest of the apparatus. This consists of a central column of brass and two disks of oak, each of three crossed layers. The column fits closely over the steel rod, and is one inch in diameter and fourteen inches high. On its lower end is a broad flange to which the larger disk is attached. The disk is nineteen inches in diameter and one inch thick, including the rim which projects about one-quarter of an inch. The upper disk is ten and one-half inches in diameter and one-half inch thick. It contains fifteen tapered holes on the circumferences of an outer and inner circle, twelve in the outer and three in the inner. The holes are about one and one-quarter inch in diameter on the upper side of the disk. Screwed to its under side is a flanged brass collar with set-screw, by which its height on the column may be adjusted. Both disks are well finished and protected against moisture by outside varnish.

[1] Made by blowing a bubble in the tube at the desired point, rubbing it off, fusing the edge of the opening left, and cutting the tube through the center of the hole.

When in use, sheet rubber covers are placed on them as a further protection. At *S* is a swivel with a clamp. It serves to hold the rubber tube through which liquid is supplied from an elevated reservoir for washing the precipitates and residues collected upon the filters. Through a small hole in the swivel at the base of the holder, the steel rod bearing the column and its disks may be oiled.

The stand, as described, was designed especially for handling the large number of ammonium phosphomolybdate precipitates obtained from the phosphorus determinations of the steel works' laboratory. The beakers are No. 1 Griffin's and the funnels two inches in diameter. Three of the fifteen beakers with which the stand may be used are placed upon the upper disk during the filtration.

III. SOLUTION WITH THE AID OF HEAT.

1. *Solution in Large Test-Tubes.*—In Fig. 4 is shown an apparatus[1] devised for use in the colorimetric determination of manganese in steel. The part of the process here concerned involves the solution of the sample in nitric acid, heating the solution to boiling, and the oxidation of the manganese it may contain to permanganic acid by continuing the boiling after the addition of lead peroxide. The samples are dissolved in ten-inch by one-inch test-tubes, eight solutions being made at once. The tubes are supported in a vertical position by a set of equi-distant clamps, modifications of a well-known form of spring-clamp. They are of stiff sheet brass, as regards the jaws, and their shafts screw into a central cylindrical block of the same material. The whole revolves about the three-eighth-inch vertical brass rod of the tripod-stand, and is supported by a similar block which may be fixed at any point on the rod by the usual set-screw. Below the clamps are eight Bunsen burners, radiating at angles of 45° from a short hollow cylinder which distributes gas to the burners. Their position on the axis is also adjustable. The burners are provided each with a stop-cock and chimney. The manner of attaching the chimney is shown at *C*. To protect the apparatus from the corrosive vapors to which it is constantly

[1] Made by Messrs. Bullock & Crenshaw, of Philadelphia, to whom credit is due for the careful execution of the idea of the apparatus as conveyed in a somewhat crude sketch prepared during the hurry of remodeling and re-equipping a laboratory. The heating apparatus shown in Fig. 5 was also constructed by the same firm.

exposed, it is varnished with special care: the polished brass parts with coach-varnish, the iron base and copper chimneys with asphaltum varnish.

By the above construction and adjustments, the solutions in the test-tubes may be brought almost simultaneously to boiling, and further treated as already pointed out. To arrest the boiling of the solutions, a slight movement of the set of clamps to the right or left suffices; if it be desired to remove only a part from the action of the flames, the tubes are drawn up in the clamps as shown in two instances in the cut.

2. *Solution in Dishes, Beakers, and Flasks.*—A few remarks of explanation in connection with Fig. 5 will make plain the construction of the apparatus here referred to. A rectangular iron stand nine inches high, twenty-five inches long, and eighteen inches wide forms its framework. This is built of an upper and lower frame, joined by legs of half-inch round bars. Low down on the legs is the lower frame, consisting of two end-pieces through which the legs pass, and three similar bars at right angles to the end-pieces. The bars of the frame are about one inch by three-sixteenths in size. Its parts are substantially riveted together. Within slight limits it may be given a higher or lower position. Screwed into each of the longer bars are four Argand burners with four-inch clay chimneys. The burners are connected by rubber tubing with the stop-cock of the one-inch brass pipe attached in front to the legs of the stand. The manner of connecting the tubing with the burners is best seen in the case of the middle row. Through the pipe in front, from either end, and its stop-cocks, gas may be supplied to any one, part, or all of the burners. The first, fourth, seventh, and tenth stop-cock, counting from the left, connect with the rear row of burners; the second, fifth, eighth, and eleventh with the middle row, etc.

The upper frame, above the burners, bears a loose asbestos pad, which forms the top of the stand. It is rimmed with sheet copper and has twelve two-inch holes, each directly over a burner. Two cross bars in the frame, parallel to those in the lower frame, prevent a sagging of the pad.

The feet of the stand are shod with rubber (stoppers bored partially through with a cork-borer) for an apparent reason.

To subserve the occasional cleaning and revarnishing to

which the apparatus, used as it is in the corroding atmosphere of the draft-chamber, must be subjected, the burners, as implied above, can be easily removed, and the gas-pipe in front detached from the clamps which support it. Besides hastening solution, this device may also be used with advantage for certain evaporations and other operations which at once suggest themselves.

The compactness of the apparatus, the ease with which the flames are perfectly controlled, due to the position of the stop-cocks, and a definite plan in their connection with the burners, the varied application of which it is capable, and its convenient portability combine to make it a most useful appliance in the laboratory.

3. An Apparatus for Use in the Determination of Sulphur in Steel by the Evolution Method.—Although excellent forms of apparatus have been proposed for the purpose indicated, a description of the combination shown in Fig. 6 is nevertheless undertaken, it seeming to the writer to have advantages which apologize for its addition to the already numerous list which might be compiled from the literature of the subject.

That part of the familiar method for the determination, which the present apparatus was designed to execute, consists in dissolving the sample of metal in hydrochloric acid, and the passage of the gases formed through an ammoniacal solution of cadmium chloride. The contact of acid and metal results at first usually in a brisk evolution of gas. This, however, soon slackens, and is then restored to the desired moderately rapid rate by the application of heat. As the metal dissolves, heating fails to maintain a steady flow of gas. At this stage of the process, hydrogen is forced into the flask in which the solution is now nearly completed, and next heated to boiling. The hydrogen serves (as need scarcely be remarked) a double purpose: the residual gases in the flasks are driven rapidly into the cadmium solution, and the liability (especially when the attention of the analyst must be divided among a number of simultaneous determinations) of the latter's "striking back" into the flask, during the boiling, is entirely obviated.

The following references to the figure will make plain the relation of the parts of the arrangement shown by it to each other and the manipulations thus roughly sketched.

The 250 cc. flasks *F*, in which the metal and acid are brought in contact, stand upon a light iron table nine inches high, seven inches wide, and twenty-three inches long. The top of the table is of asbestos board as in Fig. 5; under each flask, there is a two-inch hole through which, obviously, heat is applied to the flasks from the burners below. A stop-cock at one end of *G* enables the regulation of the supply of gas to all the burners. It is, however, essential for apparent reasons, to be able to perfectly control the supply to each burner separately. This has been effected, not by the use of the customary stop-cock, but by a slight modification of the interior mechanism of the burner. This may be seen by unscrewing the stem at the milled ring. In the center of the circle which forms the inner end of the stem, is an eighth-inch opening, and at the circumference is a pin-hole, both for admitting gas to the crown of the burner. When the parts (stem and crown) are in place, a quarter-inch disk faces the end of the stem, and is adjustable, in regard to its distance from the end, by means of the threaded shaft to which it is attached or, more accurately, of which it is a part. The shaft itself is shifted toward or from the end by the key underneath the crown. The motion toward the end at its limit brings the disk in contact with it, and more or less perfectly closes the larger opening; the pin-hole being beyond the circumference of the disk remains open.

This construction does not admit of the required perfect control of the gas-supply to the individual burner. The smallest quantity of gas that may enter produces generally too large a flame when little heat is needed, and the pin-hole prevents entirely cutting off the supply. This difficulty is resolved and the burner completely adapted to the present purpose by merely closing the pin-hole and placing a circular washer of soft leather, with a small segment removed, on the disk. If the crown and stem be now screwed together, the washer is compressed between the disk and the end of the stem, tightly closing the remaining opening in the latter. Unscrewing the parts but slightly, relieves the pressure and renews communication between the stem and the crown. The manner of manipulation with the burner thus modified is plain. Additional comment is unnecessary.

The pipe *G* is strapped to the flat bar supporting it, by strips of brass fastened with screws, and is therefore readily detached. The bar is attached to the legs of the stand in the manner described for those carrying the burners in Fig. 5, and is also adjustable as regards its level. Four spring-clamps projecting horizontally from the brass rail *R* hold the flasks securely in their places. The rail is screwed to the stand underneath the top frame. *R* further has two vertical clamps *J* similar to those just mentioned. They grasp the glass tube *H*, which is closed at one end by a rubber cap and connected at the other with a hydrogen-generator. Through *H* hydrogen is distributed to the flasks. For this purpose there is a short branch opposite each flask. The neck of the flask is closed by a rubber stopper, through which pass three glass tubes. One of these, *h*, is connected by rubber tubing with the branch to which attention was called, and reaches to the bottom of the flask. The lower end is drawn out and bent upwards slightly. By means of a compressor, the rubber tubing making the connection may be opened or closed as desired. The dropping-funnel *I*, for introducing the acid, has a wide-mouthed bulb large enough to contain the whole of the acid required for the solution; the stem holds a column of acid capable of more than overcoming the resistance offered by the solution in the cadmium chloride tubes, the ten by one-inch lipped test-tubes, *A*. The tube *E* with two bulbs conducts the gases generated in the flask into the cadmium solution in *A*. The test-tubes stand, in the rack *S*, upon a pad of sheet rubber.

Economy of space, the ease, nicety, and rapidity of manipulation possible with it, and the ability to use the device wherever the little space occupied by it may be found in the draft-chamber, are its practical features. Where a large number of determinations must be made at one time the number of stands may be correspondingly increased and controlled by one operator.

LABORATORY OF THE BLACK DIAMOND
STEEL WORKS, PITTSBURG, PA.

[CONTRIBUTIONS FROM THE ANALYTICAL LABORATORIES OF COLUMBIA UNIVERSITY.]

THE INSOLUBLE CARBOHYDRATES OF WHEAT.

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PART I—DESCRIPTIVE.

A. WHEAT STARCH.

The constitution of wheat starch has been thoroughly investigated by L. Schulze.[1] A very carefully prepared air-dried starch was employed, allowance being made in the calculations for moisture present in the sample. His results, obtained both by

[1] *J. prakt. Chem.*, 136, 311.

elementary analysis and by estimation of the dextrose formed on hydrolysis, show conclusively that the formula of wheat starch is $n(C_6H_{10}O_5)$ and not, as supposed by Naegeli, $C_{36}H_{62}O_{31}$.

The separation of starch from accompanying carbohydrates has been discussed in another paper[1] and will be referred to in speaking of analytical methods (page 302).

B. HEMICELLULOSE—PENTOSANS.

The term hemicellulose has been introduced by E. Schulze[2] to designate the carbohydrate matter yielded to boiling dilute acids by vegetable cells from which the starch has been removed. It is a portion of the cell-wall rather than of the cell contents.[3] The fact that the hemicellulose of wheat yields both arabinose and xylose on hydrolysis has already been noted.[4] In general, however, it must be said that the amount of substance which was obtained for identification was so small in proportion to that hydrolyzed as to suggest the question whether the result could be taken as proving the absence of other sugars. I decided to try a method which should not depend upon recrystallization.

Preparation of Sample.—Wheat bran[5] was extracted successively with water, saline solution, malt extract, two per cent. ammonia, cold two per cent., and boiling one-tenth per cent. sodium hydroxide. Each reagent was removed by thorough washing with water before the application of the succeeding one. This treatment removed, beside fatty and resinous matter, all of the soluble carbohydrates and starch and nearly all of the proteid matter without the use of any acid. The residue consists essentially of cell-walls.[6]

The residue from the extraction with ammonia contained, in the air-dried state, 8.30 per cent. moisture, 8.50 per cent. proteids (nitrogen × 6.25), and 3.69 per cent. ash. It yielded, on the basis of non-nitrogenous ash-free substance, 27.62 per cent. furfural (determined as described in Part II) equivalent to 50.82 per cent. pentosans.

[1] *School of Mines Quarterly*, **17**, 356.

[2] *Ztschr. phys. Chem.*, **16**, 387-391.

[3] Prof. C. Cramer, in connection with Schulze's work.

[4] Stone: *Ann. Chem.* (Liebig), **249**, 239; Steiger and Schulze: *Ber. d. chem. Ges.*, **23**, 3110; E. Schulze: *Ztschr. phys. Chem.*, **16**, 397.

[5] Bran was used instead of the whole grain because it contains all the insoluble carbohydrates of the latter and does not require the removal of so much starch.

[6] Cramer: *Loc. cit.*

The sodium hydroxide extract contained pentosans, giving the characteristic red coloration with phloroglucin in hydrochloric acid and yielding furfural when distilled with hydrochloric acid.

The air-drid residue contained 7.65 per cent. moisture, 1.25 per cent. proteids, and 3.31 per cent. ash. On the basis of non-nitrogenous, ash-free substance, it yielded 25.62 per cent. furfural equivalent to 48.13 per cent. pentosans.

Hydrolysis of the Hemicellulose.—As it was necessary to choose a somewhat arbitrary treatment, I adopted that which forms a part of the ordinary method of food analysis ; *viz.*, thirty minutes boiling with 1.25 per cent. sulphuric acid. About one-half of the substance dissolved. The residue was washed free from acid and preserved for further examination.

To the solution sufficient sulphuric acid was added to bring the total present to two per cent., and it was then boiled gently with a reflux condenser until the reducing power of the solution no longer increased (six hours). This reducing power was found to be equivalent to 91.2 per cent. of that of dextrose and showed that the solids in solution consisted almost entirely of reducing sugars. A second determination showed the organic solids in solution to have a reducing power of 91.3 per cent. of that of dextrose.

Qualitative Tests.—The solution was tested[1] for mannose with phenylhydrazine acetate, for galactose by evaporation with nitric acid, and for levulose by resorcin in hydrochloric acid. All of these tests gave negative results. Reactions of the pentoses indicated their presence in larger proportion. No direct test for dextrose, applicable under these circumstances being known, the osazone was next prepared.

Preparation of the Osazone.—This was carried out essentially as described by Gans and Tollens.[2] A part of the solution was concentrated on the water-bath until it contained ten per cent. of solids, cooled to 70°, and then mixed with an equal volume of a solution containing for each gram of carbohydrate treated, two grams phenylhydrazine hydrochloride and three grams of sodium acetate. The mixture was kept at 65°–70° for about forty-five minutes and then allowed to cool. The osazone separated as a

[1] Lippmann : *Chemie der Zuckerarten*, 338, 395, and 483.
[2] *Ann. Chem.* (Liebig), **149**, 249.

yellow iridescent precipitate which was collected, washed thoroughly and dried without recrystallization. Thus it was hoped to secure a product nearly representative of the entire solution, and whose composition should show the relative proportions of pentose and hexose present. As the yield of osazone is never quantitative, this method cannot be regarded as absolutely accurate, but, on the other hand, both dextrose and the pentoses form their osazones easily and freely under the conditions described.

Since Stone[1] has found that the osazones of the pentoses are soluble in about fifty parts of water on continued boiling, while glucosazone is quite insoluble, the proportion of the latter, if any were present, could be largely increased by dissolving away most of the pentose compound. Accordingly a part of the osazone described above was boiled for ten minutes with about forty parts water, whereby about three-fourths was dissolved. The residue was dried and analyzed as was the original preparation.

Analysis of the Osazones.—The percentage of nitrogen in each of the preparations was determined by Dumas' method with the following results:

First Preparation. — Original precipitate; *a.* 0.1716 gram yielded 26.6 cc. nitrogen at 29.5° and 764.4 mm. pressure.

b. 0.1694 gram yielded 25.8 cc. nitrogen at 20.0° and 759.4 mm. pressure.

Second Preparation.—Residue; 0.0993 gram yielded 14.8 cc. nitrogen at 21.0° and 761.0 mm. pressure.

From which we obtain:

	Nitrogen. per cent.		Nitrogen. per cent.
Original precipitate	*a.* 16.98, *b.* 17.16	Average	17.07
Residue from boiling water			16.99
Calculated for $C_{17}H_{20}N_4O_3$ (from pentose)			17.07
" " $C_{18}H_{22}N_4O_4$ (from hexose)			15.64

The hemicellulose of wheat appears then to yield on inversion only pentoses and, therefore, to consist of pentose anhydrides or true pentosans.

C. CHARACTERISTICS OF THE FIBER.

Composition and Color Reactions.—The residue from the action of sulphuric acid, after washing with water and alcohol and dry-

[1] *Am. Chem. J.*, 15, 662.

ing in the air, was of a medium brown color and loose fibrous texture. It contained 3.43 per cent. moisture, 0.65 per cent. ash, 0.25 per cent. nitrogen, and yielded 11.46 per cent. furfural. It showed well the deep magenta color (produced by lignin) when treated with chlorine and then boiled with sodium sulphite, and gave the red coloration when heated with the phloroglucin reagent (test for pentosans). No coloration was obtained on treating the fiber with a solution of fuchsin decolorized with sulphurous acid nor on boiling with anilin sulphate (tests for oxycellulose).

Reactions with Ferric Chloride and Potassium Ferricyanide.— Jute fiber, when immersed in a solution containing molecular proportions of the above reagents, fixes upon itself a large proportion of ferrous ferricyanide as a uniform deep-blue dye. This is considered by Cross and Bevan[1] as one of the most characteristic reactions of the lignocelluloses of which jute is the type.

In my experiments on the wheat fiber, I used a fresh mixture of equal volumes of aqueous solutions containing in 100 cc., one and six-tenths grams ferric chloride and three and three-tenths grams potassium ferricyanide respectively. The increase in weight of the fiber after immersion in this solution was determined by collecting in a Gooch crucible, washing well with cold water, and drying at 105°. The following quantitative experiments were made:

SERIES A.—TIME VARIED. MASSES CONSTANT.

Weight of fiber.	Volume of mixed solution.	Time of immersion.	Increase in weight.
Gram.	cc.		Per cent.
1.00	20	20 min.	9.40
1.00	20	1 hour	11.17
1.00	20	10 hours	11.16

With these proportions, then, the reaction proceeds rapidly to the maximum.

SERIES B.—TIME VARIED. MASSES CONSTANT.

Weight of fiber.	Volume of mixed solution.	Time of immersion.	Increase in weight.
Gram.	cc.	Hours.	Per cent.
1.00	20	16	11.26
1.00	40	16	21.81
1.00	60	16	30.49
1.00	80	16	36.71
1.00	100	16	46.70

[1] Cellulose, p. 124–131.

Wheat fiber has, therefore, like the typical lignocellulose (jute), the power of fixing upon itself an amount of the cyanide varying roughly with the amount exposed to its action. This reaction is very interesting as showing the similarity of the lignocellulose molecule in these tissues. It will be shown to be of value also as a test of the purity of cellulose.

D. LIGNONE CHLORIDE.

Cross and Bevan[1] have isolated a compound from chlorinated jute fiber to which they give the above name. Its composition corresponds to the formula $C_{19}H_{18}C_{14}O_9$ and is constant after fractional precipitation and when prepared under varying circumstances. It is precipitated as yellow flocks when its alcoholic solution is diluted with water.

Seventy-five grams of the fiber already described was boiled with one per cent. sodium hydroxide, washed, pressed to remove most of the water, treated with chlorine gas for one hour, washed free from hydrochloric acid, and covered with alcohol. On pressing out the alcoholic solution it was found to be of a deep golden yellow color. On concentrating and pouring into water a part only of the dissolved substance separated, as was shown by the color of the supernatant liquid. The precipitate obtained, although small (about one-half gram), corresponded in appearance with that described and on collection and analysis showed 26.7 per cent. chlorine, or just the amount required by the above formula. This seems sufficient evidence of the identity of the products.

I do not know that this compound has previously been prepared from any other source than commercial fibers, but the fact that it may be obtained from such a widely different tissue as that of the coat of the wheat kernel would indicate that this type of lignification may be general among plants of annual growth.

On the other hand, the amount recovered is too small to justify much speculation until further results are obtained.

E. CELLULOSE.

For the separation of cellulose three very different methods were tried.

1. *F. Schulze's Method.*—Thirty grams of the fiber was treated

[1] Cellulose, p. 135.

at ordinary temperature with a solution of twenty-five grams potassium chlorate in 350 cc. of nitric acid (1.10 sp. gr.). After standing seven days with occasional stirring, the strength of nitric acid was raised to 1.13 sp. gr. by the addition of concentrated acid, and the digestion continued for another seven days. Finally, the mixture was kept at about 40° for two hours, then filtered, washed free from acid, and treated on the filter with cold two per cent. ammonia as long as the filtrate was colored, and the washing finished with water and alcohol.

The sample seemed particularly resistant to this treatment so far as appearance was concerned. Instead of becoming white, it attained during the first two or three days a dull flesh color which was not materially changed during the remainder of the fortnight. The color of the dried residue was light brown, very much lighter than, but still suggesting, that of the original fiber. By repeating the treatment or increasing its severity a purer residue could doubtless be obtained but, as the yield is already less than that from the method next to be described, there seems no object in experimenting in this direction.

The residue constituted 66.0 per cent. of the original. It yielded 7.00 per cent. furfural and gave the red coloration when heated with phloroglucin. When boiled with anilin chloride it was tinged very faintly reddish, indicating a trace of oxycellulose. From twenty parts of the standard cyanide solution it absorbed 6.04 per cent. of its weight of the pigment, indicating, as comparison with the other cellulose will show, that the lignin group was not selectively attacked.

2. *Method of Cross and Bevan.*—Thirty grams fiber was boiled thirty minutes with 800 cc. of one per cent. sodium hydroxide, filtered, washed with water till free from alkali, squeezed as free from the water as possible, and then exposed in this moist condition to the action of chlorine gas in a covered beaker at ordinary temperature for one hour with occasional stirring. The color changed rapidly from brown to light lemon-yellow. At the end of the hour it was brought upon a filter and washed with water till free acid was removed, then heated to boiling with 600 cc. of two per cent. sodium sulphite and sufficient sodium hydroxide solution added to make two-tenths per cent. of the whole. The boiling was continued five minutes, the solu-

tion filtered hot and the residue washed until the washings were neutral and colorless. It is convenient to use a muslin filter and hasten the operation by squeezing out the washings. Finally the washing was finished with alcohol and the residue dried and weighed.

This process yielded 66.5 per cent. of residue of a light creamy color and free from nitrogen. It yielded 5.62 per cent. of furfural and gave a distinct coloration with phloroglucin, but not with anilin chloride. From the cyanide solution it absorbed only 0.92 per cent.

3. *Lange's Method of Fusion with Alkali.*—Bring five to ten grams of the (fat-free) substance into a porcelain crucible about three inches high with three times as much caustic potash and about twenty cc. of water. Heat with stirring in an oil-bath not above 180°, keep at this temperature (175°–180°) for an hour, cool to 75°–80°, add about seventy-five cc. hot water, cool, acidulate with sulphuric acid, make slightly alkaline with sodium hydroxide, and separate the precipitate by means of a centrifugal machine. The liquid is poured off and the cellulose washed with hot water, separating in the same way. Bring onto a filter; wash with water, alcohol and ether, dry and weigh. Incinerate and deduct the ash.[1]

Ten grams were used for each determination; the melting proceeded quietly and without troublesome frothing. The precipitate was allowed to settle by standing instead of separating by centrifugal force. Thus obtained it was of a somewhat slimy character, and the process of filtering and washing is therefore slow. This is the only difficulty of manipulation which the method presents. The cellulose dried to a white powder, the fibrous nature having been destroyed by the treatment.

Lange obtained higher results by this method than by that of Schulze, but in this case I recovered only 39.3 to 43.1 per cent. cellulose (without allowing for ash). The product yielded 3.96 per cent. furfural and gave the phloroglucin reaction, although not so markedly as did the other preparations of cellulose. Boiled with a solution of anilin salt it showed no evidence of any oxycellulose. From the cyanide solution it absorbed 0.89 per cent.

[1] *Ztschr. angew. Chem.*, *1895*, 561.

Choice of Method of Preparation.—For reasons which are mainly obvious, but which will be reviewed in speaking of analytical methods, the process of separation by means of chlorination is preferred, and cellulose thus obtained was employed in the following experiments.

Action of Strong Sulphuric Acid.—Strong sulphuric acid (100 parts sulphuric acid and seventeen parts water) dissolves pure cotton cellulose with only very slight coloration and the solution when diluted and boiled yields dextrose. E. Schulze[1] has found the same to take place with cellulose residues from other natural tissues prepared by vigorous acid hydrolysis followed by F. Schulze's reagent, although the amounts of dextrose obtained were small.

When applied to the cellulose described above, under the conditions given by Schulze, the solution was not complete and a very considerable discoloration was produced. The undissolved portion (nearly one-fifth) did not yield a measureable amount of furfural. The final product of hydrolysis of ten grams of the cellulose, converted into osazone in the usual way, gave only 1.31 grams of the latter. Its composition is shown by the following results:

a. 0.1914 gram gave 25.9 cc. nitrogen at 23.8° and 775.5 mm. pressure, equal to 15.48 per cent.; *b.* 0.1870 gram gave 24.7 cc. nitrogen at 17.0° and 771.0 mm. pressure, equal to 15.58 per cent.; average 15.53 per cent.; calculated for $C_{18}H_{22}N_4O_4$ 15.64 per cent.

The osazone is, therefore, that of dextrose and the specific products of hydrolysis of the furfural-yielding group do not appear.

Action of Cold Dilute Sodium Hydroxide.—Twenty grams cellulose was treated with 400 cc. five per cent. sodium hydroxide at room temperature with occasional stirring for two days, filtered and washed. The filtrate was light brown in color, and on neutralizing with hydrochloric acid a white precipitate was formed. I was not able to separate this precipitate quantitatively, but enough was collected to show its general resemblance to wood gum, and it gave the characteristic deep red coloration with phloroglucin. The residue constituted about eighty per

[1] *Ztschr. phys. Chem.*, 16, 414.

cent. of the amount treated. It was whiter than before treatment. A determination of furfural gave 3.34 per cent., equal to 2.67 per cent. of the original. Hence less than one-third of the dissolved substance was pentosan, and the suggestion of Hoffmeister[1] that this treatment be inserted as a step in the determination of cellulose, would seem of no value.

Chemical Nature of the Cellulose.—The term cellulose is here used in an inclusive sense to designate the strictly carbohydrate radicle as opposed to the more or less "condensed" lignin substance with which it is combined in the lignocellulose. The abnormal characteristics of this sample (property of yielding furfural and coloring phoroglucin reagent) I believe to be due to the inherent nature of the cellulose itself rather than to imperfect methods for its separation, except in the case of Schulze's method. The sample contains about ten per cent. of penta-anhydride which appears to be chemically combined with a part at least of the hexa-anhydrides (normal cellulose). It may be well now to review some of the reasons for this belief.

1. The absence of lignin groups is strongly indicated (*a*) by the fact that the repetition of the chlorination followed by treatment with sodium sulphite gave no red coloration, and very slight loss of weight, (*b*) the insignificant amount of cyanide absorbed (less than one per cent.)

2. The method of fusion with alkali, totally different in its nature, causing complete disintegration of the fiber and a much lower yield than the chlorination method, still produces a cellulose in which the abnormal characters differ only in degree from those shown by the product of the latter process.

3. The imperfect solubility in sulphuric acid and the small amount of glucosazone formed from the product of hydrolysis indicate that the cellulose is not of the normal type.

4. The proportions of substances extracted by dilute alkali show that the sample is not a simple mixture of pentosan and normal cellulose.

5. Somewhat similar characters have been found by others[2] in studying natural celluloses prepared by other methods than

[1] *Landw. Versuch-sta.*, **39**, 461.

[2] C. Schulze and Tollens: *Landw. Versuch-sta.*, **40**, 367; Hoffmeister: *Landw. Versuch-sta.*, **39**, 461; Winterstein: *Ztschr. phys. Chem.*, **17**, 391; E. Schulze: *Ztschr. phys. Chem.*, **16**, 414.

those (Cross's and Lange's methods) to whose products the above statements refer.

F. FURFURAL-YIELDING CONSTITUENTS.

Some of the facts observed in connection with this class of bodies would seem worthy of mention here. They constitute nearly or quite one-half of the seed-coat exclusive of starch and proteids—a much higher proportion than is found in woods, straws, or commercial fibers—and by far the greater part is in the form of easily hydrolyzed pentosans. The physical effect of these in rendering the tissue more tenacious and more retentive of moisture is doubtless of considerable physiological significance. It was observed in the course of this work that the samples which had not been treated with acid held about twice as much hygroscopic moisture as did those from which the pentosans had been removed, when similarly air-dried. In the case of isolated xylan, this affinity for moisture is so great as to be a most serious obstacle to its analysis.[1]

The wide distribution of furfural-yielding bodies among the different chemical groups which compose the cell-wall has been shown by the quantitative determinations mentioned above, in the original tissue, in the fiber remaining from acid treatment, in the cellulose isolated from the latter by various methods, and in cellulose which had been further treated with dilute sodium hydroxide. We have also seen that all of these specimens gave distinct pentosan reactions[2] with phloroglucin and that none of them gave distinct oxycellulose reactions with anilin salts. We therefore conclude that the furfural-yielding constituents of wheat are essentially pentosans in some form and that we commit no serious error in interpreting the amount of furfural obtained as a measure of the total pentosans present. But if we should use the term *pentosans* in this exclusive sense and stop here, it would be little more satisfactory than to include dextrin, starch, and cellulose in one group of *hexosans*. Our pentosans would con-

[1] Johnson: This Journal, **18**, 214.

[2] NOTE.—While the work was in progress the results of Cross and Bevan on the furfuroids of straws appeared (*J. Chem. Soc.*, **69**, 804-818). In view of the purple reactions with phloroglucin found by them, it was thought best to retest all the celluloses side by side with a pentose solution. Especially in the cases where the reaction was least marked, the color appeared somewhat darker and not so clear as in the pentose solution, but the difference seems to be due to the degree of heat used to develop the color. When the phloroglucin compound was precipitated by boiling and then dissolved in alcohol, no such differences were found in the alcoholic solutions.

stitute practically all of the hemicellulose, about forty per cent. of the lignin group or non-cellulose of the fiber, and about ten per cent. of the cellulose (chlorination method). It would seem much better, therefore to distinguish between those pentosans which are easily dissolved by dilute acids without materially affecting the cellulose or lignin, and those which on the other hand, are resistant to acid, or to both acid and alkaline, hydrolysis. The former are evidently not combined with hexose groups and they may be considered as true or free pentosans; the latter are apparently in chemical combination, partly in the lignin group and partly in the cellulose.

PART II—ANALYTICAL.

A. SEPARATION OF THE INSOLUBLE CARBOHYDRATES.

It is customary in cereal analysis either to be content with the results of the Weende method or to determine in addition the starch and perhaps also the furfural obtainable and calculate the latter to pentosan. The latter determination we have seen to be to a certain extent misleading since a part of the furfural comes from bodies in combination both in the cellulose and in the lignin groups and while apparently of a pentose nature, these are quite different in their properties from the true pentosans of the hemicellulose. In order to separate quantitatively the carbohydrates described in the first part of this paper, it is necessary to combine the methods best adapted to the determination of each into a single scheme. So much time was required to test the different methods and the products yielded by them that some of the details are in need of further study and the results are offered as approximate rather than absolute or final. An outline of the scheme is given and is followed by a discussion of the different steps. An application of the scheme is found in Part III.

1. *Determination of Starch.*—The results of a comparison of several methods on a series of samples specially selected to show gradations in the amount of starch present, has been published in the *School of Mines Quarterly*,[1] and abstracted in the *Analyst* for January, 1897. These results show the superiority of the malt extract method and the safety of completing the inversion of the solutions with hydrochloric acid by boiling as suggested by Hibbard,[2] instead of by long heating on the water-bath.

[1] Vol. xvii, No. 4. [2] This Journal, 17, 64.

SCHEME OF ANALYSIS USED.[1]

Five grams of the sample (previously extracted with ether) are stirred with about 100 cc. water for a few minutes, filtered, and washed.

Filtrate. — Add one-tenth its volume of 25 per cent. HCl and heat with a reflux condenser for two and one-half hours on a water-bath, or boil thirty minutes on a sand-bath.

Clarify, if necessary, and determine the dextrose present in an aliquot portion, by means of Fehling's solution, and calculate to

Soluble carbohydrates as dextrin.

Residue.—Wash into a beaker with about 100 cc. water (more if the proportion of starch is high), heat to boiling, cool partially, and invert with malt extract till starch disappears, filter, and wash.

Filtrate.—Treat as in the case of the preceding filtrate and calculate the dextrose found to

Starch.

Residue.—Boil thirty minutes with 1.25 per cent. H_2SO_4, filter, and wash with water and alcohol.

Filtrate.—Add sufficient H_2SO_4 to make 2 per cent. Boil gently with reflux condenser for six hours. Determine reducing power; calculate to pentose and thence to

Free pentosans.

Residue.—Dry and weigh. In a duplicate residue, determine proteid (and ash) and correct the weight accordingly.

Treat according to the method of Cross and Bevan, dry, and weigh the residue.

Loss of weight corrected for proteids (and ash) equals

Lignin and allied substances.

Residue, less proteid if present (and ash), equals

Cellulose.

[1] Since this work was finished, a method for the determination of carbohydrates in cereals, devised by Prof. W. E. Stone, has been published by the U. S. Department of Agriculture (Bul. 34, Office of Experiment Stations). See also this Journal for March, 1897. Another paper by Prof. Stone will be found in this issue.

2. *The Determination of True Pentosans.*—Reference has been made to the interpretation of furfural as a measure of pentosans (p. 302). It has been shown that by hydrolysis of the hemicellulose solution, pentoses only are obtained. Since, moreover, isolated pentosans are readily dissolved by dilute acids, it is evident that hydrolysis of this solution and determination of the pentosans formed must give a fairly accurate measure of the true pentosans. The kind and strength of acid used should be a subject for further study. Sulphuric acid was used in this work because the pentoses are so little altered by long boiling with it.[1] The reducing power was referred to dextrose by Allihn's table and the pentose taken as ninety-seven per cent.[2] of the amount of dextrose indicated. Pentose $\times 0.88 =$ pentosan.

3. *The Determination of Cellulose.*—The three methods compared have been described above (pp. 296, 297, 298). Exposing to chlorine after simple wetting without alkaline treatment, and then proceeding as in the chlorination method has been tried and the results are tabulated with those obtained by the regular methods. The fiber itself is also shown for purposes of comparison.

	Description of Product.				
Method.	Yield per cent.	Furfural per cent.	Nitrogen per cent.	Ferricyanide fixed; per cent.	Color.
Cross and Bevan	66.5	5.62	0.00	0.92	Light cream.
Lange	41.2	3.96	0.03	0.89	Nearly white.
Schulze.....	66.0	7.00	0.22[3]	6.04	Light brown.
Chlorination alone....	84.3	8.89	0.08	2.02	Very light brown.
Original sample.....	100.0	11.46	0.25	11.17	Brown.

It is evident that no one feature can be urged as a criterion in judging between the methods but all must be taken into consideration. Such a comparison shows the superiority of the chlorination method. It also suggests the possibility of increasing the yield without detriment to the quality of the product, by making the preceding alkali treatment less severe.

The reaction with the ferricyanide solution (p. 295) seems of considerable value in testing the purity of celluloses. When the sample increases only slightly (about one per cent. or less) in

[1] Tollens and Schulze: *Landw. Versuch-sta.*, 40, 379-384.

[2] Stone: *Am. Chem. J.*, 13, 73.

[3] Exclusive of 0.07 per cent. ammoniacal nitrogen (from the wash solution) determined by distillation with magnesia.

weight and is dyed only a bluish-green instead of a deep blue color, it is at least a very strong indication that lignin substances are not present in notable quantity. When the original fiber is dark-colored, the appearance of the cellulose will also serve as a guide, for unless this color has disappeared, it is probable that the lignin group has not been completely removed.

The significance of the furfural-yielding property of these celluloses has been discussed in the first part of this paper.

4. *Lignin and Allied Substances.*—These are determined by loss of weight when cellulose is isolated from the fiber. The general characteristic feature of the substances is their susceptibility to alkali. This is the principle upon which Lange's method is based; but since the treatment called for by the latter evidently attacks the cellulose, it is best to remove the more readily soluble portion by boiling with dilute alkali and then treat with chlorine to convert the remainder into a more easily soluble compound. The first step is also introduced in the current analytical methods, and the term lignin is usually restricted to the portion which remains with the cellulose in the "crude fiber." There is, however, no established chemical difference on which to rest such a distinction, and it is, therefore, omitted here, although the step might easily be introduced if desired.

B. DETERMINATION OF COPPER REDUCTION.

Wherever in this paper the reducing power of a solution is given, the determination has been made by adding twenty-five cc. of the solution to be tested to an excess of boiling Fehling's solution under the usual conditions of dilution, boiling exactly two minutes, collecting and estimating the cuprous oxide and taking the corresponding value for dextrose from Allihn's table. In most cases the cuprous oxide was determined as follows:[1] Collect the reduced oxide on asbestos in a filtering tube and wash well with water. Dissolve on the filter with nitric acid and wash thoroughly into a flask. To the solution add excess of sodium carbonate and dissolve the precipitate with one cc. of ammonia (0.96 sp. gr.). Titrate with a recently standardized solution of potassium cyanide until the color disappears.

The method is rapid and accurate since no other heavy metals than copper can be present. Before adopting it I checked it

[1] Lavene: *School of Mines Quarterly*, 17. No. 4.

against the electrolytic method and made a large number of experiments to show that varying amounts of sodium nitrate had no effect upon the result. After a little practice in determining the end reaction, I believe the results obtained should be as accurate as by the gravimetric methods, and much more accurate than simple titration with Fehling's solution.

C. DETERMINATION OF FURFURAL.

The method used was essentially that of the Association of Official Agricultural Chemists, but as that may not be available to all, and as some of the details were modified, it is given in full.

From two to five grams of the sample are placed in a flask with 100 cc. of hydrochloric acid of 1.06 specific gravity. The mixture is distilled and the distillate collected in a graduated receiver. Each thirty cc. lost by distillation (which should require from ten to fifteen minutes), is replaced by thirty cc. of hydrochloric acid of the strength mentioned above. Continue the process until a drop of the distillate produces no red coloration in a slip of filter paper moistened with anilin acetate. Eight to twelve distillations are usually required. Add to the distillate sufficient water to bring to a volume of 400 cc. and for every fifty cc. of water added, add 10.2 grams sodium chloride. Neutralize exactly with sodium carbonate, and add ten cc. of a solution of phenylhydrazine acetate, made by mixing twelve grams phenylhydrazine with seven and five-tenths grams glacial acetic acid and diluting to 100 cc. Stir thirty minutes and let stand in a dark closet until the following day. Filter on glass wool in glass filtering tubes six to seven inches long, removing the precipitate which adheres to the beaker by means of a feather. Dry to constant weight in an air-bath at 55° to 60° in a slow current of dry air. A partial vacuum is produced in the tube by means of suction, the supply of air being regulated by stop-cocks. Finally the precipitate is dissolved by hot alcohol, the tube dried and weighed and the loss of weight calculated as furfural hydrazone. For reducing to furfural and to pentosans the following formulas were used :

$$\text{Hydrazone} \times 0.516 + 0.0104 = \text{furfural},$$
$$\text{Furfural} \times 1.84 = \text{pentosans},$$

the factor for pentosans is obtained by averaging those of xylan and araban.

The following results obtained after only a very few preliminary trials, show what agreement may be expected without much practice.

Sample.	Weight taken. Grams.	Hydrazone obtained. Grams.	Furfural. Per cent.
A	3.860	0.836	11.46
	3.860	0.829	11.36
	3.860	0.845	11.57
B	3.870	0.393	5.54
	3.870	0.404	5.70
C	3.670	0.559	8.14
	3.670	0.561	8.17
	3.670	0.551	8.03
D	3.628	0.314	4.78
	3.628	0.311	4.74

PART III. PHYSIOLOGICAL.

INTRODUCTORY.

In questions of nutrition the proportion of food and of each of its proximate ingredients which is digested, *i. e.*, which leaves the alimentary canal and enters the physiological interior of the body, is evidently the basis of all further studies. While the different substances digested are not all utilized to the same extent, and while the undigested residue undoubtedly performs an important physiological function, these facts only serve to show the necessity of further study based upon the "digestive coefficients" and do not detract from the value of the latter when properly interpreted. Such digestive coefficients to be comparable must of course be determined by uniform methods. The analytical method used by the experiment stations in this country is published by the U. S. Department of Agriculture.[1] The work of these stations, as well as important foreign work, is periodically reviewed in the Experiment Station Record.[2] A yearly digest of the subject is included in the *Jahresbericht für Agricultur-chemie*, and it has been treated by Dietrich and Konig.[3]

It is mainly upon these experiments with animals that we are obliged to base our estimates of the digestibility of wheat and wheat products since the published results of experiments with

[1] Bul. 46, Division of Chemistry.

[2] Published by the U. S. Department of Agriculture.

[3] Zusammensetzung und Verandlichkeit der Futtermittel.

men[1] are very incomplete. But the results obtained by current methods of analysis give little information regarding the carbohydrates, this group being simply divided by an arbitrary line (sometimes considered a rough imitation of the digestive process, into "nitrogen-free extract" and "crude fiber."

Recently a number of determinations of digestibilities of total furfural-yielding substance have been reported, especially by Stone[2] and Lindsey.[3] Those of wheat bran fed to different animals (sheep and rabbits) and at different times vary from fifty-nine to sixty-four per cent.

DIGESTION EXPERIMENT.

Having studied the chemical nature of the principal carbohydrates of wheat it is interesting to find the digestibility of each as determined by an actual experiment. I was fortunate in obtaining, through the kindness of Mr. H. J. Patterson, of the Maryland Experiment Station, samples of the food and feces from an experiment conducted by him[4] upon a steer fed with wheat bran only. The total dry matter digested was 68.33 per cent. of the whole. The samples were analyzed by the method outlined above, the small amount of ash in the cellulose being neglected. The results, calculated to the dry basis, are as follows:

	Food. Per cent.	Feces. Per cent.	Per cent. Digested.
Soluble carbohydrates as dextrin	7.2	0.7	96.9
Starch	17.7	0.0	100.0
Free pentosans	17.5	18.7	66.2
Cellulose	8.5	20.2	24.8
Lignin and allied substances	11.6	23.2	36.7
Protein[5]	20.49	11.04	82.96
Ether extract[5]	6.92	12.52	42.73
Ash[5]	6.05	11.04	42.21
Undetermined	4.04	2.60	...
Nitrogen-free extract[5]	55.59	41.93	76.08
Crude fiber[5]	10.96	23.47	32.21

We see from the above that the digestibilities of the insoluble

[1] Compiled by Atwater: Bul. 21, Office of Experiment Stations, U. S. Department of Agriculture.

[2] *Am. Chem. J.*, 14, 9; *Agr. Sci.*, 5, 6.

[3] Mass. Station Report for 1894, p. 185-186.

[4] Maryland Station, Bul. 41, pp. 137-138.

[5] From Patterson's analysis.

carbohydrates range from 25 to 100 per cent. The "nitrogen-free extract" with a mean digestibility of seventy-six per cent. is composed of substances whose percentage digestibilities vary from 100 to less than forty. Even in the case of the crude fiber the digestibility of one of the constituents considerably exceeds that of the other. It must be borne in mind in this connection that the group of lignin and similar substances is divided by the current methods, part being included in the nitrogen-free extract and part in the crude fiber.

DIGESTIBILITY AND PHYSIOLOGICAL VALUE.

The final utilization of the normal carbohydrates absorbed by the healthy animal body is known to be practically complete. With lignin and pentosans or pentoses, the case seems to be different. It is held[1] that the lignin of vegetable tissues supplies directly the benzol radicle of the hippuric acid of the urine of herbiverous animals and is, therefore, but little oxidized in the body.

In the case of pentoses and pentosans whose identification is easy, the experimental methods are more direct, yet the results are very conflicting.

Ebstein[2] found that either arabinose or xylose given to men in doses of twenty-five grams, quickly appeared in the urine unchanged, and he concluded that these sugars were without nutritive value, or at least nearly so. This result has been largely quoted and its importance perhaps overestimated. Salkowski,[3] and Cramer,[4] in numerous independent experiments upon men, rabbits, and fowls, found that these sugars were mainly utilized, only about one-fifth (according to Salkowski) being given off in the urine. In many cases (according to Cramer) it was shown by killing the animals that the feeding of pentoses had caused an increased storage of glycogen in the liver. Finally Fretzel,[5] experimenting upon rabbits with xylose, has concluded that this sugar does not tend, either directly or indirectly, to promote the storage of glycogen.

[1] Meissner and Shepard: Untersuchungen über das Entstehen der Hippursäure im thierischen Organismus. Hanover, 1866. Stutzer: *Ber. d. chem. Ges.*, **8**, 575. Weiske: *Zeit. Biol.*, **12**, 24.

[2] *Archiv. pathol. Anat.*, **129**, 401; *Centrbl. med. Wissens.*, *1892*, 577.

[3] *Centrbl. med. Wissens.*, *1893*, 193.

[4] *Ztschr. Biol.*, **19**, 484.

[5] *Archiv. ges. Physiol.*, **56**, 273.

The advisability of distinguishing between starch and pentosans in food analyses is thus emphasized not only by the difference in their digestibility but also by the possible difference in physiological value of the digested portions.

CONCLUSION.

The results obtained have been discussed under the different sections. It is unnecessary to repeat them here. I would, however, offer a final word of explanation in regard to the liberty taken with the words "cellulose" and "lignin substance." These are used to designate respectively the carbohydrate, and the more or less "condensed" portions of the fiber. That either is chemically homogeneous is certainly not claimed. It is with considerable hesitation that this work is presented at this time. The amount of undetermined matter is still larger than we should wish, but those who are interested in the subject will be familiar with its difficulties, and the separations which have been made may suggest some improvement on the ordinary "nitrogen-free extract" and "crude fiber" of cereal analyses.

DISCUSSION.

Dr. Wiley: Mr. President and Gentlemen, I think the paper is one of the greatest practical, as well as theoretical, interest. As one who has been engaged for a long time in the analysis of food products, I think it is a mark of great progress to know that we are getting finally to some definite knowledge of that large class of matters which, because it was not extracted, has always been called extract. It has been rather a matter of humiliation, I think, to agricultural chemists for many years that this term has been used in the way it has been. To designate a large part of cattle and human food as nitrogen-free extract is simply to do as doctors do when they say you are suffering from malaria or grippe. It is simply using words which have not much signification, to cover up a great deal of ignorance. It is gratifying that we are now making progress in this particular line. The work in this country which has been conducted by Mr. Sherman and others, and in England by Cross and Bevan, and in Germany by Tollens and his pupils, has all been in the direction of giving us more light on these bodies. The discovery of the five-atom sugars in cattle foods, and the methods of approximately

determining them was a great step forward, and the approximate determinations of lignin and cellulose or hemi-cellulose is another step. I think Mr. Sherman should congratulate himself, rather than feel sorry for the fact that he has finally reached a point where all but three or four per cent. of a sample can be distinguished and determined. It may not be that we have yet applied the right names to these bodies. The substances may vary a little from what they seem to be, but evidently they are composed of bodies which can be separated, and their digestibility can be determined. I think we are all, perhaps, struck with the statement given here of the low digestibility of the ether extract. Here is a substance which is just as important, except in the amount of it, as the other constituents of wheat. We have been for years bringing together under the term of ether extract, a large class of bodies which were generally supposed to be fats, but we all know the digestibility of fats is much higher than the coefficient mentioned in the paper. And this leads me to say what has long been known, that the ether extracts contain a great deal besides fats, and especially are likely to be mixed with chlorophyl, or its alteration products. These products doubtless will soon be the subject also of investigation, so that we may be able to separate the so-called ether extracts into true fats and into other bodies which are much less digestible. Still we should not, I think, be misled by digestibility. Because a body disappears during its passage through the intestinal canal, is no positive proof of its assimilation. Starch, as you see, disappears almost completely, during its transit through the assimilated canal, but that is no positive proof that starch is absolutely eliminated, any more than some of the other foods, less easily changed than starch. This change begins in the mouth during mastication in the alkaline action of the saliva and is continued in a large extent in the stomach before the acidity of the stomach becomes too great. It is supposed that after the ingestion of food through the esophagus the contents of the stomach remain alkaline for some time, and the conversion of the starch goes forward with great rapidity, and is continued, perhaps, after the acidity of the stomach has been established. The digestive coefficients have value in estimating the nutritive value of food. But we do not want food that is all

digested. If we were all put on a diet that is all digested, we would all die, because it is necessary for the purpose of digestion that the peristaltic action of the bowels be secured, and there must be something to excite this action. If you digest everything you eat you will derange the health and thwart the very purposes for which feeding is practiced. And hence these undigested bodies have a value, you may call it a negative value if you will, simply because they are not absorbed. Nevertheless, they have their uses in the animal economy. So the fact that a certain food product has a digestive coefficient of 100, another of 80, another of 60, another of 30, does not furnish sufficient data on which to base any correct idea of the actual value of those foods to the animal economy. They all have a value, not only a nutritive value, but a mechanical value, and this must not be lost sight of. In fact, the methods which we practice of valuing foods is faulty, whether we consider it from the view of the physiologist simply by the amount of it which is digested, or whether we consider it from the point of view of the chemist by the amount of heat which a food will give, or whether we view it simply from the light of the physician in regard to its general effect upon the system. That is, judging a food by any one of these three standards, we reach a false conclusion. They must all be combined in order to determine the true value of the food. In determining the value of these wheat carbohydrates as foods, we must look at them from the amount of heat that they will give, that is one of the functions of food; we must look at them from their coefficients of digestibility; and we must look at them, on the other hand, from the physician's or the hygienic point of view, from their effect upon the health. Now, if in valuing food we will keep these three points in mind, we will come to a very much better conclusion than if we insist upon judging it from a single standard. We know how apt we are to think that the particular thing we are doing is the only thing in the world which is worth doing, and that everybody must come to our standard of judging any particular thing, especially a food; but this is an erroneous idea.

From the analytical point of view, too, this paper is valuable. We are now beginning to reach a point where we can discriminate among these carbohydrates, not only in a qualitative, but

also in a quantitative way. For many years the methods of so simple a determination as that of starch were very much mixed up, and in fact, it is rather difficult, even to-day, to estimate the actual quantity of starch which is present in a cereal with absolute accuracy. Of course, I do not mean with approximate accuracy. The old methods of digesting a cereal with an acid and then determining the sugar, we know to be very faulty, but the modern methods of separating the starch are, as indicated by the speaker, approximately correct. The solution of starch by diastase is one of the methods very largely practiced in our own laboratory. We also aid the solution by heating in an autoclave to a high temperature. We think we get a little better results this way than by the use of the malt extract alone. The specific rotatory power of soluble starch gives another basis for the determination, and a rapid determination of the starch present, but the method has not proved satisfactory in our laboratory. After the starch is dissolved, then we can apply the acid and convert it into dextrose. By some one of these methods the starch can be separated, practically, from the other carbohydrates present in cereal grains. When we reach the bran we are at the very beginning of the word furfurol, which, I believe, is derived from the Latin words which mean "bran oil." The fact of the derivation of this substance from the wheat bran has been known for many years. For fifty or sixty years, perhaps, the fact has been known that wheat bran would yield furfural when digested with an acid, although it was not known at the time that furfural was the splitting-up product of a five-atom sugar former. That was a matter of later knowledge. This substance is an old one, and yet it comes to us now under new forms and in new lights. The most difficult part of the problem, as indicated by the speaker, was the final separation of the lignins and cellulose, and allied bodies, and perhaps there is a great deal to be done yet before we reach final results. These bodies are so near each other and run into each other by such almost imperceptible gradations that it requires the highest degree of analytical skill, as well as of chemical research and investigation, to devise means by which they can be practically separated from one another. Therefore I think this Society should welcome all investigations of this nature, and I hope it

will not be long before this paper appears in full in the columns of the Journal.

Mr. M. L. Griffin: Mr. President and gentlemen, I have been very much interested in this paper presented this morning. It is in line with work which I have been connected with for some time, and as Mr. Stone and Dr. Wiley have said, any information on this subject is of great utility to this Society, to chemists, and to the chemical world. The difficulties of separating the bodies which have been referred to, are extreme, and any information, though incomplete, is certainly welcome.

We digest 110 cords of wood daily for paper-making at Mechanicville, N. Y., which illustrates how intimately the subject of this paper connects itself to the commercial world, not only in the digestion of carbohydrates by the animal economy but also to manufacturing industries. I venture to say that the commercial practice of separating cellulose from the intercellular and incrustating matter of wood or carbohydrates generally is very much ahead of the science of the subject.

The difficulty of making a laboratory separation of the components of wood or any carbohydrate resulting from plant growth lies in the fact that the more highly organized or developed molecules are a growth by continuous processes. If you will picture to your minds the growth of a tree from the coursing of the life-giving sap just under the bark where the latest growth is taking place to the heart of the tree, you will find a continuous development or growth with no clean cut gradations. This is the reason why it is so difficult to make definite separations within narrow limits.

Reagents which will dissolve incrusting and intercellular substances in wood are not without effect upon the cellulose itself.

This brings us to the methods laid down in books for the determination of cellulose in woody tissues. In brief they are summed up in alternate treatment of the samples over the water-bath, with an alkali and an oxidizing agent as chlorine or bromine. This is repeated until you get "pure cellulose."

You who have tried this, know how tedious it is and how worthless the results are, simply for the reasons given above. As technical chemists we know that a practical test for the

determination of cellulose in woody tissues by using small digesters in which we may subject the material to high temperature and pressure with suitable chemicals for a short time, will make a much clearer separation of cellulose and with less destructive effect. This is the method I employ for technical purposes.

We also know that some chemicals are more destructive to the cellulose than others in this connection. A chemical treatment in which the materials are not allowed to oxidize during the process of digestion, has a much less destructive effect on the cellulose, and produces a much more durable fiber for paper-making. The importance of this increased "yield", as manufacturers call it, is very apparent. The completeness of the separation of the cellulose from all foreign matter is equally important and desirable from every point of view.

I trust I have said nothing which will deter any chemist from undertaking work along this line. Our knowledge of the insoluble carbohydrates is very limited, and while we may only approximate the results we desire, there is a vast field here for highly valuable and useful service.

We may congratulate ourselves on the presentation of this paper by one of our members.

President Dudley: I would like to ask Mr. Sherman if the coefficient of digestibility of the whole wheat can be obtained from this paper?

Mr. Sherman: No, it was just an experiment on the bran. The digestibility of the whole sample was 68.33 per cent. In regard to Mr. Griffin's remarks on the analytical methods, and especially for cellulose, I think that we will have to design our methods largely, at least as yet, according to the object we have in view. As I indicated, I do not think that we can say that cellulose, the cellulose we get from any given fiber, will be $C_6H_{10}O_5$, and nothing else; in fact I am quite sure we cannot say that. What I have attempted was the separation on chemical lines, as far as possible, and as I am very free to admit, I did not get any pure cellulose ($C_6H_{10}O_5$) by any of the methods, and the methods that gave the purest cellulose gave too low a yield. I think the chlorine method is much the best, because it attacks the lignin group selectively, and does not disintegrate the whole as the strong alkali usually does. This cellulose

consists of both hexose anhydrides and pentose anhydrides; I am not prepared to say whether that would be suitable for paper-making or not; I should think likely not. So that what we arrive at when we try to work from a purely chemical standpoint might be entirely unsuited to a given commercial case.

IMPROVEMENTS ON DR. SQUIBB'S VOLUMETRIC METHOD FOR ESTIMATING ACETONE.

By Lyman F. Kebler.

Received February 13, 1897.

IN the December[1] number of this Journal Dr. Squibb gave a a translation of MM. J. Robineau[2] and G. Rollin's method for estimating acetone, as well as a modification of the process by himself. Both methods consist essentially in mixing an aqueous acetone solution with a strongly alkaline potassium iodide solution and converting the acetone into iodoform by means of a titrated solution of sodium hypochlorite, the end reaction being determined by means of a bicarbonated starch solution.

Dr. Squibb kindly sent me his modification last summer. Prior to that time I had used Messinger's process exclusively. I have not applied Robineau and Rollin's method to any extent, but have studied and worked with Dr. Squibb's modification of the same quite considerably.

The two latter methods will meet with two objections; first, a *pure acetone*, and second, the tedious, time-consuming drop end reaction. Pure acetone is not so readily prepared. I have not been able to secure acetone that assayed more than 99.73 per cent. of pure material, by either Messinger's[3] process or the one presently to be described. This small quantity may have volatilized in course of the work, but the loss would be practically constant for all the methods; consequently, the basis of calculation would be 100, when in reality it is less. Grant that absolutely pure acetone can be made, it is not readily secured when desired.

I have modified Dr. Squibb's method so that both the pure

[1] This Journal, 18, 1068; *Ephemeris*, 4, 1759.
[2] 1893: *Mon. Sci.*, (4), 7, Pt. I, 272.
[3] 1888: *Ber. d. chem. Ges.*, 21, 3366.

acetone and the drop end reaction are eliminated. The reactions involved in this process may be represented by the following equations:

$$Cl_2 + 2KI = I_2 + 2KCl.$$
$$I_2 + 2KOH = KIO + KI + H_2O.$$
$$CH_3COCH_3 + 6KIO = CH_3COCI_3 + 3KOH + 3KI.$$
$$CH_3COCI_3 + KOH = CHI_3 + KC_2H_3O_2.$$
$$KIO + KI + 2HCl = I_2 + 2KCl + H_2O.$$
$$KIO_3 + 5KI + 6HCl = 3I_2 + 6KCl + 3H_2O.$$
$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6.$$

There may be some difference of opinion concerning the primary reactions involved, but the basis of calculation is not affected.

The solutions required for this process are as follows:

1. A six per cent. solution of hydrochloric acid.

2. A decinormal solution of sodium thiosulphate.

3. An alkaline potassium iodide solution. To prepare, dissolve 250 grams of pure potassium iodide in distilled water and make up to one liter. Dissolve 257 grams of sodium hydroxide, purified by alcohol, in distilled water and make up to one liter. Allow the insoluble part to subside and mix 800 cc. of the clear solution with the liter of potassium iodide.

4. Sodium hypochlorite solution, about four-fifths normal, or containing from two and six-tenths to three per cent. of available chlorine. To prepare this solution, intimately mix 100 grams of bleaching powder (thirty-five per cent.) with 400 cc. of water. Dissolve 120 grams of crystallized sodium carbonate in 400 cc. of hot distilled water, and immediately pour the latter into the former. Cover the vessel and allow to cool. Then decant the clear liquid, filter the remainder, and to the filtrate add enough water to make up to one liter. To each liter add twenty-five cc. of sodium hydroxide solution, specific gravity 1.29.

5. An aqueous acetone solution containing from one to two per cent. of acetone. This is prepared by weighing the acetone in a beaker containing water, transferring to a graduated cylinder, rinsing the beaker with water and making up to a definite volume.

6. Bicarbonated starch solution. Treat 0.125 grams of starch with five cc. of cold water, then add twenty cc. of boiling water,

and boil a few minutes, cool, and add two grams of sodium bicarbonate.

Having prepared the above solutions, place twenty cc. of the alkaline potassium iodide solution into a suitable flask, add ten cc. of the diluted aqueous acetone; or weigh if greater accuracy is desired; mix well, and run in from a burette, while rotating the flask, an excess of the sodium hypochlorite solution, insert the stopper quickly and shake well for one minute. After agitating, render the mixture acid, by means of the hydrochloric acid solution, add, while rotating the flask, an excess of sodium thiosulphate solution, mix well and allow the mixture to stand a few minutes. Then add the starch indicator and re-titrate the excess of sodium thiosulphate. It is best to add a drop of the sodium hypochlorite in excess and adjust the final reading by means of the sodium thiosulphate.

The relation of the sodium hypochlorite solution to the sodium thiosulphate solution being known, the percentage of acetone can readily be calculated from the above data. One atom of available chlorine will liberate one atom of iodine from the potassium iodide of the alkaline solution, or one cc. will liberate just enough iodine to make one cc. of the same normal strength as the sodium hypochlorite solution originally was; therefore by reading the number of cc. of sodium hypochlorite solution consumed as so many cc. of iodine solution of the same normal strength, we reduce the calculation to the basis of iodine. One molecule of acetone (58) requires three molecules of iodine (759) to form one molecule of iodoform. Expressing it in the form of a proportion, letting y equal the amount of combined iodine and x equal the amount of acetone, we have: $759 : 58 :: y : x$, or $x = y\,\frac{58}{759}$, or $x = y.\,0.07641$.

Example of Calculation.—Ten cc. of the acetone solution, containing one gram of the solution to be analyzed required 14.57 cc. of $N \times 0.806$ sodium hypochlorite solution, which formed 14.57 cc. of iodine solution of the same strength; or combining we have $\frac{14.57 \times 0.806 \times 0.1265 \times 0.07641}{\text{one gram of solution}} = \text{amount of acetone}$ $= 11.351$ per cent.

On comparing Messinger's and Dr. Squibb's with the modified

method proposed, using the same solutions, the following results, in per cent. were obtained:

	Messinger.	Squibb.	Kebler.
Pure acetone	99.69	99.95	99.73
Residue 80° C. and above	20.00	19.67	20.39
Purified acetone by fra'tion	99.03	99.00	99.41
Commercial acetone	96.23	96.00	96.63
" "	98.00	97.83	97.93
" "	94.30	94.00	94.46
" "	94.80	94.70	94.81
" "	97.12	96.23	96.42
" "	94.93	94.80	94.39
" "	96.88	96.56	96.79
" "	97.32	97.28	97.45
" "	90.74	89.03	90.51
" "	98.82	96.11	98.62
" "	92.32	92.20	92.94
Wood alcohol	14.61	14.49	14.78
" "	11.81	11.73	12.00
Crude wood alcohol	11.23	11.00	11.42

The above table clearly shows that the results obtained by Dr. Squibb's process are a trifle too low, notwithstanding the fact that its basis of calculation gives it some advantage. The method is represented to give satisfactory results for ordinary work and that it certainly does. The difficulty with the process is in the end reaction. According to some experiments made by me, it is necessary to have present a larger excess of the active agent, to bring about the completed reaction, than the end reaction allows.

The iodoform reaction with ethyl alcohol is an endothermic one, consequently its presence does not interfere with the estimation of acetone, which does not require the presence of external heat to bring about the reaction.

LITERATURE ON ESTIMATING ACETONE NOT IN THE BODY OF THE ARTICLE.

1880. G. Krämer: "Ueber die quantitative Bestimmung des Acetons im Methylalcohol." Ber. d. chem. Ges., 13, 1000.

1888. E. Hintz: "Zur quantitativen Bestimmung von Aceton im Methylalcohol, Holzgeist und Aceton," Ztschr. anal. Chem., 27, 182.

1890. Fr. Collischonn: "Ueber die gebräuchlichen Methoden zur quantitativen Bestimmung des Acetons," Ztschr. anal. Chem., 29, 562.

1890. H. Hubert: "Zur quantitativen Bestimmung des Acetons im Harn," Ztschr. anal. Chem., 29, 632, from Neubauer und Vogel: "Anleitung zur Analyse des Harns," 9 Auf., 471.

1890. L. Vignon: "Dosage de l'acétone dans l'alcool, méthylique et dans les méthylènes de dénaturation," Compt. rend., **110**, 534.

1890. G. Arachequesne: "Dosage de l'acetone par l'iodoforme," Compt. rend., **110**, 642; Ztschr. anal. Chem., **29**, 695.

1894. N. Savelieff: "Ueber die Vorkommen von Aceton im Mageninhalt bei Erkrankung des Magens," Berliner klin. Wochenschrift, No. 13; und Maly's Jahresberichte über die Fortschritte der Thierchemie," **24**, 352, 1896; Ztschr. anal. Chem., **35**, 507.

1896. Chr. Geelmuyden: "Ueber die Messingersche Methode zur Bestimmung des Acetons," Ztschr. anal. Chem., **35**, 503.

1896. M. Klar: "Zur Bestimmung des Acetons in de naturirungs-Holzgeist und Rohaceton," Die chem. Ind., **19**, 73; Ztschr. anal. Chem., **35**, 595.

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[CONTRIBUTIONS FROM THE CHEMICAL DIVISION, U. S. DEPARTMENT OF AGRICULTURE, NO. 25.]

DETERMINATION OF POTASH AND PHOSPHORIC ACID IN FODDERS.

CONTRIBUTED BY H. W. WILEY.

Received January 26, 1897.

IN the comparative analyses of soils during the past three years we have grown a great number of pot cultures and determined the mineral plant foods in the resulting crops. The following modified potash method, devised by Mr. K. P. McElroy, while not sacrificing accuracy, has made it possible for one analyst to determine the potash, often in duplicate, in more than ten samples a day. Since the quantity of the crop harvested from a poor soil is often small, it is desirable that the phosphoric acid and potash be determined in the same sample.

The method in use for the determination of potash in feeding stuffs, in the laboratory of the United States Department of Agriculture is a simple modification of the ordinary Lindo-Gladding method, as prescribed by the Association of Official Agricultural Chemists. It is as follows:

Burn eight grams of the substance over a low flame to approximate whiteness. Burning after addition of sulphuric acid does not give more potash than burning alone, and it is more troublesome. Transfer the ash to a 200 cc. flask, using about fifty cc. of water, add five cc. of strong hydrochloric acid and place on the steam-bath for an hour, or boil from five to ten minutes. Add a little iron chloride to precipitate all phosphoric acid as fer-

ric phosphate, then ten cc. of strong ammonia and then from five to ten cc. of ammonium carbonate solution (200 grams per liter of the commercial salt). Replace on the steam-bath and heat for an hour, and allow to stand over night. Complete the volume to the 200 cc. mark with water and shake three times at intervals of five or ten minutes. Grease the inside of the neck of the flask and pour its contents on a dry folded filter. When all is transferred to the filter and run through, wash down the neck of the flask with a little water, put the funnel into the flask, and stand aside till the filter dries. Then roll up the filter and push down into the flask. Add dilute nitric acid, digest, make volume up to the mark, and use an aliquot part for the determination of phosphoric acid.

Transfer fifty cc. of the filtrate containing the potash, equivalent to two grams of material, to a platinum dish, cover and heat on the steam-bath till evolution of gas ceases. Remove the cover and rinse it and the sides of the dish with a stream from the wash bottle. Evaporate to dryness and heat in an air-bath till all water is removed in order to avoid loss by decrepitation in the subsequent ignition. Heat over a low gas flame till the bulk of the ammonium chloride is removed, cool and add one cc. of sulphuric acid (1 : 1), then heat on a hot plate till fuming begins, then over a flame till all the sulphuric acid is driven off and the residue in the dish is white. Every portion of the dish should reach a low but distinct red heat, the bottom first and then the sides. The reason for the preliminary driving off of the bulk of the ammonia as sal-ammoniac is that ammonium sulphate melts and sputters, involving danger of loss. Cool the dish and add one or two drops of strong hydrochloric acid, then from fifty to seventy-five cc. of water, washing down the sides of the dish with a jet from the wash bottle. Add platinum chloride solution in amount equivalent to 150 mm. of metallic platinum, for materials not containing over four per cent. of potash. Very few reach this limit. Evaporate on the water-bath as usual and take up with alcohol of eighty (volume) per cent. Filter through a Gooch crucible, keeping the insoluble material in the dish as far as possible. Wash with four more portions of alcohol, decanting through the crucible each time. Finally rinse down the sides of the crucible with a stream of alcohol from a

wash bottle. Cover the residue in the dish with the half-saturated solution of ammonium chloride prescribed in the official method for the determination of potash, and stir thoroughly. Decant through the Gooch crucible and treat with five or more portions of sal-ammoniac solution, decanting through the crucible each time. Finally wash into the crucible with eighty per cent. alcohol. When the transfer is complete, rinse the sides of the crucible thoroughly and finally fill it twice with alcohol, of course, constantly filtering with a vacuum. Dry for an hour at 100° and weigh.

Pour about 150 cc. of boiling water through the weighed Gooch crucible. If the platinum potassium chloride is not wholly dissolved, again bring the filtrate to a boil and pour through once more. Store this filtrate finally in a large flask, containing aluminum clippings, to reduce the platinum. Bring a fresh portion of water (150 cc.) to a boil and pour through the Gooch crucible. Remove the crucible from the vacuum apparatus, wipe, and dry in an air-bath, with good ventilation, for two hours, at 110°. Weigh once more. The loss in weight is the double chloride. The second portion of hot water is used to dissolve the double salt in the next crucible operated upon, after being once more brought to a boil.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

PERIODIDES OF PYRIDINE.[1]

BY P. F. TROWBRIDGE.

Received February 1, 1897.

Pyridine Methyl Pentiodide, $C_5H_5N.CH_3.I.I_4$.—This preparation has been reported,[2] but the present method of preparation is of interest. It was obtained in two experiments, when pyridine was added to an alcoholic solution of iodine containing methyl iodide. The precipitate of the pyridine tetriodide[2] was filtered off and the liquor set aside for partial evaporation. The crystals obtained were purified by recrystallizations from alcohol. Melting-point 44.5° C.

	Calculated for $C_5H_5N.CH_3I.I_4$.	Found. 1.	2.
Total iodine[3]	87.06	86.24	87.19
Titrated iodine	69.65	69.64	69.21

[1] Continuation of paper by Prescott and Trowbridge. This Journal, 17, 859.
[2] This Journal, 17, 859.
[3] This Journal, 17, 867, for methods of analysis.

Pyridine Methyl Heptiodide, $C_5H_5N.CH_3I.I_6$.—A provisionally named octaiodide was reported,[1] but it is very probable that it was a mixture of the heptiodide with some free iodine. In the present experiment, the iodine was taken in great excess to the pyridine methyl iodide; *i.e.*, sufficient for twelve atoms of additive iodine. The pyridine methyl iodide and the iodine were mixed when in the form of hot saturated alcoholic solutions. The mixture was kept hot for fifteen minutes. A heavy dark-green oil formed, which was rapidly separated. This became a crystalline solid at about 20° C. and melted when warmed above 30° C. Insoluble in water, but soluble in dilute alcohol, from which it crystallizes in fine green needles, which are fairly stable. Melting-point 26° C.

	Calculated for $C_5H_5N.CH_3I.I_6$.	Found. 1.	2.
Total iodine	90.40	90.36	90.23
Titrated iodine	77.48	77.31	78.21

The liquor from the above was found to contain the pentiodide not entirely pure.

At the present writing we have not succeeded in preparing a higher periodide of pyridine methyl iodide. When pyridine methyl iodide is heated in sealed tubes to 125° C. with an alcoholic solution of iodine, the pentiodide is formed. When the same mixture is heated to 175° C. ethyl iodide is formed and no definite periodide could be isolated. When pyridine methyl iodide and iodine are heated in tubes to 200° C. without the addition of alcohol, the heptiodide is formed. This product was purified by recrystallization from alcohol. Melting-point 26.5° C. Reported as 2 above.

When pyridine and iodine are heated to 175° C. the tetriodide is formed.

Pyridine Ethyl Pentiodide, $C_5H_5N.C_2H_5I.I_4$(?).—When pyridine, iodine, and alcohol are heated in tubes to 175° C., a pasty mass is formed having a carbonaceous odor. Definite black crystals were obtained by treatment with alcohol. Melting-point 83° C.

	Calculated for $C_5H_5N.C_2H_5I.I_4$.	Found.
Total iodine	85.41	86.32
Titrated iodine	68.33	68.59

The corresponding methyl compound melts at about 44° C.[1]

[1] This Journal, 17, 859.

This ethyl compound should melt below 44° C., as the normal ethyl iodide melts at a much lower temperature than the methyl compound.[1] It is quite possible that ethyl iodide is first formed, which combines with the pyridine; and then, under the pressure and heat, the Ladenburg reaction takes place and ethyl pyridine hydriodide tetriodide, $C_5H_4(C_2H_5)N.HI.I_4$, is formed. Pyridine ethyl triiodide (described later in this paper) also melts at 51° C. Pyridine ethyl pentiodide must melt at a lower temperature. Further investigation will be made of this preparation.

To find, if possible, the limit of iodine addition to pyridine methyl iodide, the following series of experiments was made. A definite amount of carefully purified pyridine methyl iodide, $C_5H_5N.CH_3I$, was dissolved in a small amount of alcohol, and to this a cold saturated alcoholic solution of iodine was added. The amount was taken so that in (1) there was just sufficient iodine for one atom of additive iodine; in (2) just enough for two atoms of additive iodine; etc. In this series of experiments the solutions were not warmed. All were treated at the temperature of ordinary summer weather.

1. No crystals formed in twenty-four hours. On cooling in salt and ice an abundance of red needle-like crystals was obtained. These were purified from alcohol. Melting-point 49° C.

	Calculated[2] for $C_5H_5N.CH_3I.I.$	Calculated for $C_5H_5N.CH_3I.I_2.$	Found.
Total iodine.....	72.91	80.14	79.26
Titrated iodine.....	36.46	53.43	52.11

2 and 3. Crystals formed at once, and upon purification gave handsome, overlapping, reddish-brown plates. Melting-point 50° C.

	Calculated for $C_5H_5N.CH_3I.I_2.$	Found.[2] 2.	3.
Total iodine.....	80.14	79.46	79.59
Titrated iodine.....	53.43	53.09	53.08

4. A heavy green oil formed at once, which became a semi-solid green mass upon standing. This was purified from alcohol. Short greenish needles were obtained. Melting-point 44° C. From the liquor, after removal of the oil, crystals were

[1] This Journal, 18, 91.
[2] This Journal, 17, 860.

obtained, which, upon purification, gave the reddish-brown plates. Melting-point 50° C.

	Calculated for $C_5H_5N.CH_3I.I_2$.	Calculated for $C_5H_5N.CH_3I.I_4$.	Found. Oil.	Liquor.
Total iodine.....	80.14	87.06	86.12	79.40
Titrated iodine..	53.43	69.65	66.47	53.13

5. A dark-green oil formed at once, forming crystals upon purification. Analysis gave 85.73 per cent. of total iodine and 66.76 per cent. of titrated iodine. From the liquor more oil was obtained, which also gave crystals upon purification. Analysis gave 80.17 per cent. of total and 63.80 per cent. of titrated iodine. In both the above cases the crystals were not sharply defined, nor were they of definite melting-points. Theory as $C_5H_5N.CH_3I.I_2$ gives 84.33 per cent. of total and 63.25 per cent. of titrated iodine.

6. Results very similar to those in (5) were obtained, except no crystals whatever could be secured from the first oil. Green needles were obtained from the liquor. Iodine found, 86.30 per cent. total and 70.08 per cent titrated.

7. The green oil which formed at once gave the dark-green needles upon crystallization from alcohol. Melting-point 44° C. Found 86.50 and 68.56. From the liquor dark-green crystals were obtained. Melting-point 45° C. Found 85.92 and 70.08.

8. A dark-green oil formed at once. This was purified. Found 86.31 and 69.51. In the liquor long dark-green needles formed on standing over night. These were analyzed without further purification. Melting-point 44.5° C. Found 86.57 and 68.24.

9. As in 8. Melting-point 44.5° C. Found from oil 86.88 and 69.17; from liquor 86.81 and 68.99.

10. The dark-green oil would not crystallize from alcohol. The liquor gave very long (three inches) dark-green needles. These were analyzed without further purification. Melting-point 44° C. Found 86.26 and 68.87.

The following table gives a brief summary of the results in the series above described:

		Melting-point.	Total iodine. Found.	Theory.	Titrated iodine. Found.	Theory.	Calculated for
1		49	79.26	80.14	52.11	53.43	$C_5H_5N.CH_3I.I_2$
2		50	79.46	80.14	53.09	53.43	$C_5H_5N.CH_3I.I_2$
3		..	79.59	80.14	53.08	53.43	$C_5H_5N.CH_3I.I_2$
4		44	86.12	87.06	66.47	69.65	$C_5H_5N.CH_3I.I_4$
4	liquor	50	79.40	80.14	53.13	53.43	$C_5H_5N.CH_3I.I_2$
5		..	85.73	84.33	66.76	63.25	$C_5H_5N.CH_3I.I_3$
5	"	..	80.17	84.43	63.80	63.25	$C_5H_5N.CH_3I.I_3$
6		..	....	....	....	....	
6	"	..	86.30	87.06	70.08	69.65	$C_5H_5N.CH_3I.I_4$
7		44	86.50	87.06	68.56	69.65	$C_5H_5N.CH_3I.I_4$
7	"	45	85.92	87.06	70.08	69.65	$C_5H_5N.CH_3I.I_4$
8		..	86.31	87.06	69.51	69.65	$C_5H_5N.CH_3I.I_4$
8	"	44.5	86.57	87.06	68.24	69.65	$C_5H_5N.CH_3I.I_4$
9		44.5	86.88	87.06	69.17	69.65	$C_5H_5N.CH_3I.I_4$
9	"	..	86.81	87.06	68.99	69.65	$C_5H_5N.CH_3I.I_4$
10		..	....	....	....	....	
10	"	44	86.26	87.06	68.87	69.65	$C_5H_5N.CH_3I.I_4$

In further studying the limits of iodine addition with pyridine methyl iodide, another series of experiments was made, in which pyridine was added to an alcoholic solution of iodine containing methyl iodide. The iodine was so taken that (1) gave iodine for one additive atom, (2) for two, etc., temperature conditions being the same as in the preceding series. In all cases there was formed at first the pyridine tetriodide, which was rapidly separated by filtration and the liquor set aside for evaporation and crystallization. The products obtained were purified by recrystallization and then carefully analyzed.

(1) and (2) gave a mixture of the pyridine methyl diiodide and triiodide. (3) gave the triiodide in most excellent conditions of purity. (4) and (5) gave the pentiodide very pure.

From the above series of experiments we must conclude that, at ordinary temperature and with small amounts of iodine, the triiodide is usually formed, and with larger amounts of iodine the pentiodide; and this latter is the highest periodide that will form of pyridine methyl iodide at ordinary temperature, no matter how much iodine be used. Some of the preparations are evidently mixtures of the triiodide and the pentiodide. There is no satisfactory evidence of the formation of a pyridine methyl tetriodide.

Pyridine Hydriodide, $C_5H_5N.HI,H_2O$.—White needle-like

crystals, soluble in water and alcohol, insoluble in ether, melt at about 268° C. with some decomposition. Upon standing, the crystals become brownish in color and after a few days give off pyridine. Dilute hydriodic acid freshly distilled from red phosphorus was added to pyridine diluted with water. The crystals were obtained by partial evaporation and then cooling. These were purified by crystallizing from water and drying over sulphuric acid.

0.4501 gram gave 0.4728 gram silver iodide, or 0.2554 gram iodine, or 56.74 per cent. iodine.

Theory for $C_5H_5N.HI.H_2O$ = 56.34 per cent.
Theory for $C_5H_5N.HI$ = 61.25 per cent.

Pyridine Hydriodide, $C_5H_5N.HI$.—This preparation has the same properties as that just described. It is made by adding freshly distilled hydriodic acid, sp. gr. 1.96, to pure pyridine cooled in a mixture of salt and ice. The pure white crystals formed at once and were purified by washing repeatedly with absolute ether. After being thus purified they do not take up a molecule of water when recrystallized from water. Neither the salt purified by washing with ether nor that crystallized from water loses an appreciable amount on being heated for six hours at 100° C.

Iodine found before drying.	Iodine found after drying six hours.	Theory for $C_5H_5N.HI$.
61.21	60.88	61.25
60.93	60.65	....
61.00	....	....

Pyridine Hydrogen Diiodide, $C_5H_5N.HI.I$.—Dark-brown short needles, perfectly stable, slightly soluble in water, very soluble in alcohol. Melting-point 188°–192° C. Crystallizes from absolute alcohol as brown overlapping plates. This preparation was made (1) by treating pyridine with hydriodic acid containing some free iodine, and then allowing to stand; (2) by adding an alcoholic solution of iodine to pure pyridine hydriodide in the cold.

	Found.		Calculated for $C_5H_5N.HI.I$.
	1.	2.	
Total iodine.....	75.66	75.75	75.97
Titrated iodine.....	37.32	37.95	37.98
	....	37.93	....
	....	37.94	....

Hollow Crystals of the Pyridine Hydrogen Diiodide.—The liquor from the first crystallization of the $C_5H_5N.HI,H_2O$, was treated with an alcoholic solution of iodine (not a great excess), and allowed to stand for twenty-four hours. A large bulk of crystals was obtained, fully fifty grams. They were reddish-brown hexagonal hollow prismatic crystals of very uniform size and many of them fully two inches long. Melting-point 188°–191° C. These crystals are the pyridine hydrogen diiodide but not quite pure. Analytical results are about one per cent. too low, both in total and titrated iodine. When these hollow crystals are recrystallized from alcohol the pure diiodide is obtained in fine needle-like crystals. I have tried repeatedly to reproduce the hollow crystals, but without success. Hollow crystals have been reported by Kebler.[1]

Pyridine Hydrogen Pentiodide, $C_5H_5N.HI.I_4$.—Stable, very dark, brownish-black, short crystals, melting-point 78°–82° C. Obtained (1) from the liquor of the heptiodide described below, by evaporation and several recrystallizations from alcohol; (2), by dissolving iodine in hydriodic acid, warming, and adding a calculated quantity of pyridine. Crystals form and are purified from alcohol, in which they are very soluble.

	Found.		Calculated for $C_5H_5N.HI.I_4$.
	1.	2.	
Titrated iodine.....	71.09	69.91	71.01
Total iodine.....	....	87.66	88.77

Pyridine Hydrogen Heptiodide, $C_5H_5N.HI.I_6$.—Lustrous green scales, fairly stable, soluble in alcohol, melting-point 63°–64° C. Hydriodic acid was added to pyridine and then heated on the water-bath. To this a hot saturated alcoholic solution of iodine was added. An abundance of crystals was obtained upon cooling. Purified by recrystallization from alcohol.

	Found.	Calculated for $C_5H_5N.HI.I_6$.
Total iodine	92.23	91.71
Titrated iodine	78.65	78.67

Not being successful in any of the previous experiments in making pyridine hydrogen triiodide, a series of experiments was started, from which it was hoped to obtain the desired periodide. Pure pyridine hydriodide was dissolved in dilute alcohol, and iodine in alcoholic solution was added. (1) contained

[1] *Am. J. Pharm.*, 67, 602.

iodine sufficient for one-half atom of additive iodine, (2) for one atom, (3) two atoms, (4) three atoms, (5) four atoms, (6) five atoms, (7) six atoms, (8) seven atoms, (9) ten atoms, and (10) fifteen atoms.

In (1) to (6) no heat was used, in the others the solution of pyridine hydriodide was heated and the iodine added as a hot saturated alcoholic solution.

(1). After several crystallizations the pure $C_5H_5N.HI.I$ was obtained in needles one-half inch long.

(2). Same as (1).

(3). Same as (1), but impure.

(4) and (5). $C_5H_5N.HI.I_4$, but impure.

(6). $C_5H_5N.HI.I_4$, pure.

(7). $C_5H_5N.HI.I_6$, pure.

(8), (9), and (10). $C_5H_5N.HI.I_6$, fairly pure in each case.

Thus far we have been unable to make the triiodide, $C_5H_5N.HI.I_2$. The corresponding periodides of the methyl and ethyl series are very easily made.

Pyridine Ethyl Triiodide,[1] $C_5H_5N.C_2H_5I.I_2$.—To 23.4 grams pure pyridine ethyl iodide dissolved in a small amount of alcohol, 12.6 grams of iodine dissolved in alcohol were added. No crystals formed on standing twenty-four hours, lightly covered, but after a second twenty-four hours, several large clusters of crystals were formed. These are bluish-black, thin, rhomboidal, overlapping plates. Melting-point 51° C.

In a second preparation a greater quantity of iodine was taken and the pure crystals obtained free from adhering oil by several recrystallizations. Melting-point 51° C. In a third and fourth preparation the above periodide was made in the attempt to make pyridine ethyl chloride periodide. A water solution of pyridine ethyl iodide was shaken with a slight excess of freshly precipitated silver chloride until the filtrate gave no test for iodine. This filtrate was treated with a potassium iodide solution of iodine. A heavy black oil formed, which was carefully separated and placed in tightly stoppered bottles. Owing to other work, these stood for three months. The oily products had become crystalline with some adhering oil. The crystals were very compact, hard, lustrous, and greenish-black.

[1] This Journal, 17, 862.

Careful tests showed entire absence of chlorine. They were recrystallized from absolute alcohol, when lustrous, greenish-black, overlapping plates were formed. Some of these plates are fully one inch long, with very definite angles. Melting-point, (3), 52° C., (4), 51° C.

	Found.				Calculated for $C_5H_5N.C_2H_5I.I_2$.
	1.	2.	3.	4.	
Total iodine	77.91	77.68	78.33	....	77.85
	77.27	77.57	....	....	....
Titrated iodine ...	50.77	51.83	52.42	52.15	51.90
	51.48	51.91	51.80	51.80	....
	51.06	....	51.86	....	....

Work is being continued on periodides of quinoline piperidine and mixed perhalides of pyridine and quinoline.

Molecular Weight Determinations.—Much difficulty has been experienced in determining the probable molecular composition of the pyridine periodides. Since alcohol is such a ready solvent for them and heat so readily decomposes them, it was deemed advisable to try the vapor-tension method of Will and Bredig.[1] We find that this method is not at all applicable to the perhalides, but as a check on our own work, we very easily confirmed Will and Bredig's work on nitrobenzene.

The freezing-point method was tried, using nitrobenzene, formic acid, glacial acetic acid, and phenol. None of these solvents seem to decompose the perhalides, but phenol is the only solvent that gives sufficient deviation of the freezing-point.

	Found.	Theory.
$C_5H_5N.HI.I$	387	
	375	
	386	333
	398	
$C_5H_5N.CH_3I.I$	398	
	334	347
$C_5H_5N.C_2H_5I.I_2$	403	
	423	487
$C_5H_{11}N.CH_3I.I_2,H_2O$	496.8	497.5

$C_5H_5N.CH_3I.I_4$. No accurate results.

It is of much significance that two different diiodides, having but one atom of additive iodine to one atom of normal iodine, are clearly found to be monopyridine compounds, the same as those with even numbers of additive iodine. It would appear, therefore, that in the diiodides one of the two iodine atoms exer-

[1] *Ber. d. chem. Ges.*, **22**, 1084.

cises an even valence, as in $C_5H_5N<^{R}_{I-I}$, or perhaps $C_5H_5N<^{R}_{I=I}$. With the higher perhalides the burden of experiment points very strongly to the formation of compounds having only an even number of additive halogen atoms. The structure may be[1] $C_5H_5N<^{R}_{I<^{I-I}_{I-I}}$, etc., at all events indicating uneven valence for all halogen atoms. It is quite probable that all the pyridine perhalides exist in monopyridine molecules.

If there be an analogy between the perhalides of the tertiary amines and the ammonium salts of the oxyacids of chlorine, then the structure may be $\equiv N<^{R}_{(I=I)-I}$, $\equiv N<^{R}_{(I=I)-I<^{I}_{I}}$, etc., where $(I=I)=O$. In this case the single additive halogen would be divalent and a substitute for oxygen, *i. e.*, $\begin{matrix}H\\H\\H\end{matrix}\!\!\equiv N<^{H}_{O-Cl}$ and $\equiv N<^{R}_{I-I}$. In the mixed perhalides to be reported in a later paper, the single additive halogen is of more frequent occurrence.

I wish to express my thanks to Professor A. B. Prescott, to whom I have gone for advice and under whose general supervision the work has progressed; also to Messrs. O. C. Diehl[2] and R. E. Knapp for their assistance in the laboratory.

ANN ARBOR, MICH., Jan. 23, 1897.

MODIFICATION OF THE THALLEOQUIN TEST FOR QUININE.

BY F. S. HYDE.

Received February 18, 1897.

IT is extremely important for the success of this test that the reagents employed should be dilute. Some authorities give the quantity of each reagent necessary, without stating the proper dilution, thereby causing much inconvenience.

The light green coloration produced on porcelain by contact of the quinine salt with weak bromine or chlorine water and

[1] This Journal, 17, 780.

[2] This is the beginning of Mr. Diehl's work upon "Foundations for the Estimation of Alkaloids, Conducted for the Committee of Revision of the U. S. Pharmacopeia," by Prof. A. B. Prescott. The next following work has been upon "Mixed Perhalides of Pyridine and Piperidine," now nearly ready for publication.

ammonia is not nearly so striking as the brilliant emerald green color obtained by using dilute solutions in a test-tube.

Usually, the analyst deals with unknown quantities, or mere traces, but, for experiment, it will be found convenient to use from three to five milligrams of the quinine salt for each test. (With larger amounts there is a tendency to form bulky precipitates.)

For example, place three to five milligrams (0.003–0.005 gram) quinine sulphate in a test-tube and add about five cc. distilled water. Acidulate with *one* drop (not more) of dilute sulphuric acid (1 : 4) which immediately dissolves the quinine sulphate with a blue fluorescence. An excess of the acid should be avoided.

At this point various authorities recommend the addition of weak bromine or chlorine water; but the writer has found that if a clear, filtered solution of calcium hypochlorite (bleaching powder) be substituted for the bromine or chlorine water, the results will be more satisfactory so far as certainty and brilliancy of the test are concerned.

The points to be observed are as follows: After acidulation with one drop of sulphuric acid (1 : 4), the hypochlorite solution is added through a small filter to the quinine solution in the test-tube, until the blue fluorescence just disappears, and the solution acquires a faint golden tint; then add a few drops of dilute ammonia (1 : 3) when a clear emerald green color should appear. (Thalleoquin test.)

The tint, thus produced, seems to be more brilliant than that obtained through the agency of bromine water.

On the addition of a slight excess of dilute sulphuric acid to this green solution, a blood-red tint will be produced which may be considered confirmatory. This is not always the case, however, when bromine water has been used in the preliminary operation.

Potassium or sodium hypobromite is not applicable on account of the strong alkali which tends to precipitate the white quinine base and thus interfere with the brilliancy of the test. Chlorinated soda (Labarraque's solution) likewise gives uncertain results, the tints varying from yellowish-green to violet.

LABORATORY BROOKLYN HEALTH DEP'T,
February 17, 1897.

COMPOUNDS OF METALLIC HYDROXIDES WITH IODINE.

By Theodore Rettie.

Received March 1, 1897.

SCHLAGDENHAUFFEN[1] describes a method for the quantitative determination of magnesium in a solution containing barium, strontium and calcium without previously removing these metals. He employed a reagent prepared by adding iodine to a two per cent. solution of potassium hydroxide, in sufficient quantity to produce a golden yellow solution. This reagent gives, even with very dilute solutions of magnesium salts, a dark, reddish-brown precipitate. An apparently similar precipitate was obtained by the same author by adding iodine, dissolved in potassium iodide solution, to a solution of a magnesium salt and then cautiously adding potassium hydroxide solution. Excess of the latter reagent entirely decolorizes the precipitate, leaving magnesium hydroxide. The nature of the brown precipitate does not seem to have been determined by Schlagdenhauffen, and therefore it appeared of interest to examine it with a view to ascertaining if it is of constant composition.

In order to prepare quantities of the precipitate, solution of magnesium sulphate was mixed with enough solution of iodine in potassium iodide to impart to it a dark brown color. Potassium hydroxide solution was then added in sufficient quantity to produce a bulky precipitate, leaving the solution still dark-brown. The brown precipitate, when filtered off and sucked as dry as possible, if washed with hot water, loses all its color and decreases considerably in bulk, leaving a white residue of magnesium hydroxide. The washings are colorless, neutral to test papers, and give the reactions of magnesium and of iodides. Cold water acts on the precipitate in a similar manner, but only very slowly. If washed with water saturated with iodine, no iodide is dissolved out, as was determined by titrating the aqueous solution of iodine before and after the washing. When exposed to the air the dry precipitate loses iodine very slowly; dried in a vacuum no iodine is lost. This was proved quantitatively by determining the ratio of iodine to magnesium in some of the freshly precipitated substance, and then in the same precipitate when dried in a vacuum; in both cases the ratio was the same.

[1] *J. Pharm. Chem.* (4), 27, 375.

A portion of the moist precipitate gave on analysis :

0.0330 gram silver iodide, or 0.0178 gram iodine, and 0.0771 gram magnesium pyrophosphate, or 0.0168 gram magnesium.

Therefore I : Mg : : 1 : 4.9.

Dried in a vacuum, same precipitate gave 0.0289 gram iodine by titration, and 0.0452 gram magnesium oxide or 0.0272 gram magnesium.

Therefore I : Mg : : 1 : 4.9.

Chloroform, ether, alcohol, and potassium iodide all extract a little iodine from the dried precipitate, but none of them extract the whole of it. Sulphurous acid and sodium thiosulphate both decolorize the precipitate completely. The precipitate dissolves completely in acids, giving a solution colored brown by free iodine. On heating the dry substance to 100° C. water is given off, but no iodine; this fact was proved by a determination of the ratio of iodine to magnesium before and after heating. On ignition in a sublimate tube, the substance, previously heated to 100° C., gives off water and then iodine, and if ignited strongly enough leaves pure magnesia. Advantage was taken of this latter reaction to obtain a quick method for determining the iodine and magnesium.

The substance was weighed in a platinum boat, ignited in a piece of combustion tubing, having one end drawn out and passed through an India rubber stopper so as to dip into a solution of sulphurous acid contained in a small flask. A current of air being sucked through the apparatus, the iodine is absorbed in the flask and can be determined either by adding dilute nitric acid to the sulphurous acid solution and precipitating with silver nitrate, or by employing instead of sulphurous acid a known quantity of standard thiosulphate solution and titrating back with standard iodine. The residue from the ignition in the tube contains a small quantity of iodine, which is given off on stronger ignition, leaving pure magnesia. The results of analyses of five different preparations are given below.

A. The ratio of iodine to magnesium was determined in some freshly precipitated substance. In a given weight there was found 0.0902 gram silver iodide, or 0.0487 gram iodine, and 0.1650 gram magnesium pyrophosphate, or 0.0361 gram magnesium.

I : Mg : : 1 : 3.8.

B. Freshly precipitated gave ratio I : Mg :: 1 : 4.9 (as above). Dried in a vacuum,

	Per cent.
0.1008 gram substance gave 0.0452 gram MgO	= 44.84
0.0289 gram I	= 28.67
H_2O by difference	= 26.49
	100.00

I : Mg :: 1 : 4.9.

MgO : H_2O :: 1 : 1.06.

C. The precipitate dried in a vacuum over sulphuric acid was heated to 100° C. in a steam cupboard till constant in weight. The iodine and magnesium were determined by the ignition method described above. The water was determined directly by ignition in a combustion tube, the iodine being absorbed by a red hot silver spiral and the water collected in a sulphuric acid tube.

Substance taken = 0.1185 gram.

	Per cent.
MgO = 0.0616 gram	= 51.98
I = 0.0307 gram	= 25.90

Water. Substance taken, 0.1990 gram.

H_2O = 0.0430 gram	= 21.93
	99.81

I : Mg :: 1 : 6.3.

H_2O : MgO :: 1 : 1.05.

D. Dried *in vacuo* over sulphuric acid.

Substance taken = 0.0610 gram.

	Per cent.
MgO = 0.0300 gram	= 49.18
I = 0.0166 gram	= 27.21
H_2O by difference	= 23.61
	100.00

I : Mg :: 1 : 5.6.

MgO : H_2O :: 1 : 1.07.

As it seemed probable that the low percentage of iodine in "C" might be due to loss of iodine on heating to 100° C., the ratio of iodine to magnesium was determined in the next preparation (E) both before and after heating to 100°.

E. This precipitate was produced under slightly different conditions from the former ones. A very large excess of iodine was employed and the precipitate was left standing for twenty-four hours in contact with an excess of iodine. The precipitate when filtered off and dried in a vacuum had a dark greenish-black appearance and yielded, on pounding up, a very dark purplish brown powder.

Precipitate dried in a vacuum.

Substance taken = 0.3584 gram.

	Per cent.
MgO = 0.1185 gram	= 33.06
I = 0.1759 gram	= 49.07
H_2O by difference	= 17.87
	100.00

I : Mg :: 1 : 2.1.

MgO : H_2O :: 1 : 1.2.

Precipitate heated to 100° C. for three hours.

Substance taken = 0.3303 gram.

	Per cent.
MgO = 0.1130 gram	= 34.21
I = 0.1686 gram	= 51.04
H_2O by difference	= 14.75
	100.00

I : Mg :: 1 : 2.1.

H_2O : MgO :: 1 : 1.03.

Collecting the above results we get the following ratios :

A. I : Mg :: 1 : 3.8.

B. I : Mg :: 1 : 4.9, MgO : H_2O :: 1 : 1.06.

C. I : Mg :: 1 : 6.3, H_2O : MgO :: 1 : 1.05.

D. I : Mg :: 1 : 5.6, MgO : H_2O :: 1 : 1.07.

E. I : Mg :: 1 : 2.1, H_2O : MgO :: 1 : 1.03.

These results show that the precipitate is simply magnesium hydroxide with a variable quantity of iodine carried down with it, giving a body resembling the lakes. Aluminum acetate gives a similar precipitate, but not so stable as the magnesium one. Aluminum sulphate, however, will not react thus. Moist magnesium hydroxide (freshly precipitated and washed), on shaking up with iodine solution, takes up iodine, although more slowly than that precipitated in presence of the iodine, while it does not seem capable of taking up so much.

On trying the action of potassium hydroxide in presence of iodine on the salts of the other metals of the magnesium group, colored precipitates were formed with zinc and cadmium salts. Glucinum sulphate gave a dark-brown precipitate which dissolved upon standing; when more potassium hydroxide was added a precipitate of hydroxide formed. With strong solutions of calcium and strontium salts, a very peculiar reaction took place, a dark, greenish-brown precipitate being produced, which changed to reddish-brown, and on standing for a short time dissolved completely. Excess of potassium hydroxide gradually took the color out of the precipitate, but much more slowly than with magnesium. Barium salts do not react in this way at all. Lithium chloride behaves in a somewhat similar manner to calcium salts; a dark-brown precipitate is formed, which soon dissolves. On adding a little more potassium hydroxide, the same precipitate again forms and again dissolves up.

The cadmium and zinc precipitates are much more stable than the above. The cadmium precipitate (from cadmium nitrate), when filtered off and washed with water saturated with iodine, is very gelatinous and of a dark purple brown color; on drying in a vacuum it gradually loses its color till it becomes a pale buff, when no further change takes place. On heating this buff-colored powder in a platinum boat in a combustion tube, water and iodine were given off, leaving a brown residue of cadmium oxide; the oxide was dissolved in nitric acid and tested for iodine; none present.

The formation of the zinc precipitate depends on the salt used and also on the strength of the solution; neither the sulphate nor chloride gives the precipitate while the acetate does. When a solution containing forty grams zinc acetate per liter is employed, a brown flocculent precipitate is formed, which does not change on standing. If the brown precipitate be filtered off and dried in a vacuum, it gives off all its iodine, leaving a white powder. In a solution containing fifteen grams zinc acetate per liter, the brown flocculent precipitate at first formed takes up more iodine on standing with a large excess of iodine and becomes crystalline and of an olive green color. This green precipitate when filtered off and washed with water is not decomposed, but if left exposed to the air in a moist state rapidly turns

brown, losing iodine. Dried in a vacuum the precipitate is not decomposed. The dirty green powder thus obtained is not so stable as the magnesium compound; it smells of iodine, and when left exposed to the air gradually becomes white. When heated to 100° in a steam cupboard iodine vapor is given off. On ignition in a platinum boat in a combustion tube, water and iodine are given off first, then a small white sublimate of zinc iodide. As this prevented any speedy method of determining the zinc in the substance, the ordinary method of precipitation with sodium carbonate was employed. The difficulty of washing and drying large precipitates without decomposing them necessitated the employment of small quantities for analysis.

A. Substance taken = 0.0949 gram.

	Per cent.
ZnO = 0.0500 gram	= 52.68
AgI = 0.0485, or I = 0.0250 gram	= 27.61
Water determined directly (as in magnesium compounds.)	
Substance taken = 0.1724 gram.	
H_2O = 0.0294 gram	= 17.05
	97.34

I : Zn :: 1 : 2.9.

ZnO : H_2O :: 1 : 1.4.

B. Substance taken = 0.0616 gram.

	Per cent.
ZnO = 0.0982 gram	= 48.80
AgI = 0.1150 gram, or I = 0.0621 gram	= 30.88
H_2O by difference	= 20.32
	100.00

I : Zn :: 1 : 2.5.

ZnO : H_2O :: 1 : 1.9.

C. Substance taken = 0.3409 gram.

	Per cent.
ZnO = 0.1731 gram	= 50.77
AgI = 0.2035 gram, or I = 0.1094 gram	= 32.09
H_2O by difference	= 17.14
	100.00

I : Zn :: 1 : 2.4.

ZnO : H_2O :: 1 : 1.8.

The excess of water above what would correspond to zinc oxide is evidently due to incomplete drying, as the substance cannot be heated to 100° without decomposition.

I would take this opportunity of expressing my cordial thanks to Professor Crum Brown and Dr. Leonard Dobbin for many important suggestions received during the investigation.

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VARIATIONS IN THE COMPOSITION OF RED LEAD.[1]

BY DURAND WOODMAN.

IN the manufacture of red lead and orange mineral, the color is ordinarily the property of first importance, since its chief use is as a pigment; and except so far as the color is dependent on the degree of oxidation, the latter is not the subject of special consideration.

For certain purposes, however, the degree of oxidation is important, and having occasion to examine a large number of samples of red lead from various sources, I adopted the method of digesting in saturated solution of normal lead acetate, by which the litharge in excess of that in combination as Pb_3O_4 (or $2PbO.PbO_2$) is dissolved out and separated. The samples were all examined qualitatively for anything which might be considered as adulteration, but otherwise neglecting the small amounts of silica, lime, oxide of iron, and carbon dioxide normal to the commercial article, for the preliminary and approximate tests. In this way a series of results was obtained showing a variation in the amount of actual red lead from 41 to 92 per cent., as given in the tabular statement.

No. or mark.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Red lead, Pb_3O_4	51.0	56.0	72.0	75.0	41.0	90.0	89.5	70.0	87.0	89.5
Litharge, PbO.....	49.0	44.0	28.0	25.0	59.0	10.0	10.5	30.0	13.0	10.5

No. or mark.	517.	140.	C.	BWL.	C.	BWL.	C.	L. B.	BWL.	L. B.
Red lead, Pb_3O_4	60.0	84.0	50.0	60.0	58.0	77.0	66.0	90.0	73.5	87.5	92.0
Litharge, PbO	40.0	16.0	50.0	40.0	42.0	23.0	34.0	10.0	26.6	12.5	8.0

The figures for red oxide are in most instances a little high because of the insoluble impurities which have not been determined and deducted, but the point which it is desired to bring out, is the large amount of monoxide in some samples,

[1] Read before the January meeting of the New York Section of the American Chemical Society.

which has escaped oxidation; is separable by the lead acetate treatment; and which I believe, from the ease with which it is so separated, has no part in the chemical constitution of red lead. It seems to be simply an admixture and a measure of the incompleteness and imperfection of the roasting or oxidizing process.

In this connection some interesting data are given in Gmelin's Handbook, Vol. v, p. 118, concerning the degree of oxidation corresponding to the length of time on the hearth of the reverberatory furnace in the roasting process.

"Red lead" prepared from massicot with

1 firing	of 24 hours,	contains	50.0	per cent.	red lead	(Pb_3O_4).				
2 firings	"	"	"	"	52.1	"	"	"	"	"
3	"	"	"	"	58.1	"	"	"	"	"
4	"	"	"	"	64.1	"	"	"	"	"
5	"	"	"	"	66.2	"	"	"	"	"
8	"	"	"	"	74.8	"	"	"	"	"

Red lead from "white lead" with 3 firings of 24 hours contained 95.3 per cent. red lead (Pb_3O_4).

The analyses which I have made seem to show that little or no improvement has been made in the methods of manufacture from the standpoint of more complete oxidation.

The lead acetate treatment has a special interest in that it is one of the methods used by Dumas to demonstrate the individuality of the red oxide as a true chemical compound, although his results led him to the supposition that it was a sesquioxide [Pb_2O_3] rather than a chemical union of the monoxide and peroxide.

The separation of the lead monoxide and red lead by this method is quite sharp, prolonged digestion in the acetate solution failing to produce any appreciable change in the weight of red lead.

By the usual methods of analysis, depending on the decomposition of the red lead into peroxide, which remains insoluble, and monoxide, which dissolves, no distinction is made between the monoxide in combination according to the formula $2PbO.PbO_2$, and that which is present in excess and so easily removed by the acetate solution. An analysis of red lead is generally stated as follows:

	Per cent.
Peroxide, PbO_2	26.4
Litharge, PbO	69.7
Impurities	3.5
	99.6

Since the formula Pb_3O_4 is accepted, and this compound is the essential part of a red lead, no matter what may be the views held as to whether the excess of PbO is a mere admixture, or in weak chemical combination; it would seem more satisfactory for commercial work to state an analysis as follows:

	Per cent.
Peroxide of lead, PbO_2	26.4 per cent.
Equivalent to red lead	75.6
Lead monoxide (litharge)	20.5
Impurities	3.5
	99.6

If the acetate method is used, we obtain the red lead figure directly; if methods yielding the peroxide or its equivalent, the amount of peroxide found should be multiplied by the factor 2.866 to give the corresponding quantity of red lead.

DISCUSSION.

In regard to the lead monoxide removable by digestion of red lead in solution of lead acetate, Professor Sabin said that in making a cement of litharge and glycerine, considerable inert material, as sand or powdered glass, might be mixed with it without affecting the setting qualities; while on the contrary, red leads would not make a cement when mixed with glycerine. This would seem to indicate that the litharge is not in the same condition as if in simple admixture.

SODIUM PEROXIDE AS A THIRD GROUP REAGENT.

BY S. W. PARR.

Received February 1, 1897.

SODIUM peroxide as a reagent has properties of a very unusual and striking character. These properties are no less valuable than peculiar, and indicate for this substance a prominent place in analytical work. The immediate object of this paper is to note the advantages and adaptability of sodium peroxide to qualitative analysis. By this means its numerous characteristics can be best illustrated. The specific data indi-

cating its use in certain lines of quantitative analytical work will be given later. The methods herein set forth have been employed in this laboratory during the past year by large classes in qualitative analysis. This practical test of the processes involved has abundantly demonstrated their value.

In the ordinary procedure for the separation of the metals the greatest difficulty arises in the third or iron group. These complications may be briefly enumerated as follows:

(*a*) The separation of zinc in the presence of chromium.

(*b*) The unsatisfactory separation of cobalt and nickel from the other members of the group by the action of dilute hydrochloric acid on their sulphides.

(*c*) The variations arising from the presence of phosphates, etc.

It is not necessary to enlarge upon these difficulties. The one most commonly ignored in methods as usually outlined and yet a very serious obstacle, is the one designated under (*a*). Zinc and chromium enter into a combination which to a very large extent resists the action of ammonia and ammonium salts. The use of barium carbonate to obviate this difficulty is cumbersome. By use of sodium peroxide we may oxidize the chromic compounds present to sodium chromate, and thus completely eliminate it as a factor in any precipitation likely to be employed, excepting of course such as would involve a reduction and return to the condition of a chromic salt.

The method of procedure is as follows: The solution should be slightly acid. A small porcelain spoonful of the peroxide is slowly sifted in with constant stirring. The solution is then heated to complete the decomposition of the peroxide and finally boiled for some minutes after the oxygen seems to be all driven off. The completeness of the oxidation may be easily tested by filtering from any insoluble constituents, acidifying, boiling, and making ammoniacal. A precipitate may be aluminum or unoxidized chromium. Filter and wash free from all sodium chromate, redissolve in a little nitric acid and treat as before with a small amount of sodium peroxide. A yellow coloration is due to the chromium which escaped oxidation by the first treatment. However, if properly conducted, the first operation should be complete. Similarly, the insoluble residue on the filter, if suspected of being a zinc-chromium compound, may be

washed free from chromate, dissolved in dilute nitric acid, and treated again with the peroxide. The only condition so far governing the completeness of the transformation to the chromate form is the necessity of starting the oxidation with the chromium entirely in solution. Precipitated chromium hydroxide will undergo this transformation, but less readily, and especially if the precipitate is the double one of zinc and chromium. Hence the advisability of beginning the oxidation with the solution containing some free acid, preferably nitric. The quantity of free acid is immaterial, less than one cc. being sufficient. It should be noted, however, that the amount of sodium peroxide should cause the solution to pass quite beyond the neutral condition since the oxidation is only partial while in the acid state. It might be expected that the moment the addition of sodium peroxide passed the neutral point the precipitation of chromium would commence and the completeness of the oxidation be lessened in consequence, but I have not found this to be the case. The oxidizing action of the peroxide is so pronounced that it precedes the precipitating action, hence the reason for using the dry sodium peroxide. A cold saturated solution of the peroxide will operate but incompletely. Hydrogen peroxide will also act similarly, but even less completely than the solution of sodium peroxide. For obvious reasons also the operation is performed on the solution before heating, and it is better to shake the powder in gradually than to drop the reagent in at once.

We are ready now to note the effect of such treatment as above indicated, upon the other members of this group, assuming that any or all may be present, including cobalt and nickel. The results are as follows:

(*a*) Aluminum compounds are in solution in the form of sodium aluminate, not different from the ordinary result from using sodium hydroxide in excess. It is assumed of course that the sodium peroxide has exceeded the free acid in sufficient amount to provide sodium hydroxide in excess.

(*b*) Zinc is similarly in solution as zincate.

(*c*) Iron precipitates as a very dense, reddish-brown precipitate, the exact composition of which is being made a matter of investigation. The precipitation is complete, no re-solution being effected upon boiling. The filtration is performed with great

facility. The precipitate is almost insoluble in concentrated nitric acid; soluble in dilute acids on heating. If phosphates are present, none are precipitated with the iron, but all pass through and are found in the filtrate.

(*d*) Manganese behaves exactly as iron, precipitating presumably as the hydrated dioxide, $MnO_2 \cdot xH_2O$, having all the properties of that compound as to color, solubilities, etc. Similarly also, phosphates are not precipitated. It should also be noted that from this precipitate can most readily be obtained the delicate test for the presence of manganese by formation of permanganic acid by means of nitric acid and lead peroxide or Pb_3O_4.

(*e*) Cobalt precipitates also a black hydrated cobaltic oxide with solubilities the same as in the case of iron and manganese. No phosphate is precipitated with the cobalt. The precipitate, in conjunction with dilute acid and potassium iodide, liberates free iodine, imparting an intense blue to starch solution. This latter property, however, is common to the precipitates of iron and manganese under (*c*) and (*d*).

(*f*) Nickel precipitates, as the ordinary green nickelous hydroxide, $Ni(OH)_2$, easily soluble in acid, either concentrated or dilute. As to phosphates, in the case of nickel, if present in large amounts, small quantities are found in the precipitated nickel. A re-solution and reprecipitation with sodium peroxide, however, eliminates all the phosphate from the precipitate. The behavior of nickel in thus precipitating as the nickelous compound indicates for its higher form of oxidation a less degree of stability than exists in the case of cobalt. This property suggests the readiest and most delicate method for the detection of nickel, even in the presence of the three precipitates enumerated above, thus: boiling this precipitate of nickel with bromine water converts it at once into the black nickelic hydroxide, which has the property of decomposing potassium iodide with water alone, no acid being required, as in the case of iron, manganese, and cobalt. It is necessary, of course, to boil off the free bromine, which is readily accomplished. The action upon a potassium iodide starch solution is very marked.

The above facts suggest a method for the iron group which is

indicated by the following table. It is given here to illustrate the adaptability of some of the well-known but more positive and satisfactory tests for the several metals.

The precipitate obtained in the ordinary method by means of ammonium hydroxide and ammonium sulphide contains, as hydroxides and sulphides, iron, manganese, cobalt, nickel, aluminum, zinc, and chromium, and is brought into solution by means of ten to fifteen cc. of concentrated nitric acid with heat. Nearly neutralize with sodium hydroxide, then sift in slowly with stirring sodium peroxide in excess. Boil.

Precipitate A contains iron, manganese, cobalt, and nickel.

(*a*) Test for iron by dissolving a small portion of the precipitate in dilute hydrochloric acid and adding potassium thiocyanate. The blood red coloration is due to ferric thiocyanate.

(*b*) For manganese, to five cc. water add five cc. concentrated nitric acid and five to ten grams Pb_3O_4. Stir into the warm mixture a little of the precipitate and let stand. A purple solution is permanganic acid.

(*c*) In absence of iron or manganese, stir a little of the precipitate into dilute hydrochloric acid and add solution of potassium iodide and starch. In presence of iron and manganese use the bead test.

(*d*) Boil some of the precipitate with bromine water till all bromine is expelled, add water and solution of potassium iodide and starch, $Ni(OH)_3 + KI = Ni(OH)_2 + KOH + I$, imparting the blue to the solution.

Solution A contains all the aluminum, zinc, and chromium. The yellow color is evidence of chromium. Acidify with hydrochloric acid, boil, and add ammonium hydroxide.

Precipitate B consists of aluminum hydroxide, and any chromium hydroxide that may have escaped oxidation. Dissolve in nitric acid and repeat the precipitation with sodium peroxide, or apply the blowpipe and cobalt test for aluminum.

Solution B contains zinc and chromium.

(*a*) Test for zinc by adding to a portion a few drops of potassium ferrocyanide. A heavy white precipitate indicates zinc.

(*b*) If further verification of chromium is needed, make the solution acid with hydrochloric acid and boil with a little alcohol added. The chromium reverts to the green chromic chloride.

In the presence of phosphates the method so far employed has been as follows: Upon dissolving the precipitate from the ammonium sulphide in concentrated nitric acid a very little of the solution is tested for phosphoric acid in the usual manner. If

present, granulated tin is added and the boiling continued. Filter from the insoluble tin phosphate, make ammoniacal, reprecipitate with ammonium sulphide, and proceed as with phosphoric acid absent. Any method not involving the use of tin and depending upon the non-formation of the phosphates of iron, manganese, and nickel, is as yet unsatisfactory. Having removed the barium and strontium with sulphuric acid before the precipitation with ammonium sulphide, the oxidation and precipitation by means of sodium peroxide may be performed as usual, but before filtering, the solution is made acid with acetic acid and boiled a little further and filtered. The filtrate now may contain besides the aluminum, zinc, and chromium, the nickel which is readily soluble in acetic acid, and the calcium and magnesium which has been brought along by means of the phosphoric acid. A little of the cobalt, however, dissolves with the acetic acid and a solvent has not been found thus far for the calcium phosphate and nickel hydroxide that will not dissolve traces of the other three metals of the precipitate.

One other application to qualitative analysis may be mentioned as having proved valuable. In testing for acids a ready method for distinguishing between carbon dioxide and sulphur dioxide when both are present is found in the use of a solution of sodium peroxide. Conducted into this solution, the above gases form sodium carbonate and sodium sulphate respectively. With lime-water the solution will give a copious precipitate if the carbonate has been formed, and with an acidulated solution of barium chloride the sulphate test is obtained.

Many other features incidental to the properties above outlined have developed, mainly of interest in quantitative methods. It is hoped that the data will be of sufficient value to warrant further notice.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY.]

THE QUANTITATIVE DETERMINATION OF CARBOHYDRATES IN FOOD STUFFS, II.

BY W. E. STONE.

Received March 24, 1897.

IN a preceding number of this Journal a plea was made for a more definite knowledge of the constituents of the "nitrogen-free extract" of food stuffs, and a method of analysis was proposed for differentiating between the various carbohydrates included in that term.

The analytical data there presented were in part obtained in an investigation upon the carbohydrates of wheat and maize, done by the writer and published as Bulletin 34 of the Office of Experiment Stations, U. S. Department of Agriculture. This method of estimating carbohydrates was employed there for the first time, and was necessarily imperfect in some of its details. This was notable in the starch determinations, which gave results much too low. This error was noticed by the author, but too late to be corrected in the original paper. It was corrected, however, in the article referred to in the March number of this Journal, in which the scheme for analysis was first described in detail. The error consisted in the employment of too dilute acid for the hydrolysis of the starch products, previously rendered soluble by the action of malt extract upon the material under examination. Originally one cc. of concentrated hydrochloric acid to 100 cc. of the solution under treatment was employed. As modified on pp. 188–189 of the March number of this Journal, ten cc. of concentrated hydrochloric acid are added to 100 cc. of the solution and the whole heated for one hour in boiling water. This correction was made as the result of a comparative study of the strength of acid and duration of treatment necessary to completely change diastatic starch products into dextrose. At the time of going to print, the writer had been unable to complete the treatment of all the materials under investigation, according to this revision. The original starch data obtained with more dilute acid, were therefore presented and attention was called to their derivation on p. 193.

It is now possible to present the results obtained from the

original samples, using the corrected method of hydrolysis described on pp. 188–189, as follows:

NORMAL STARCH DISSOLVED BY MALT EXTRACT.

	Per cent.
Wheat I	57.62
Wheat II	56.27
Wheat flour I	67.99
Wheat flour II	67.76
Maize	65.45
Bread from Wheat I	53.54
Bread from Wheat II	53.62
Bread from Flour I	64.81
Bread from Flour II	64.12
Bread from Maize	61.64

It will be noted that the amounts of starch have been increased from fifteen to twenty per cent. over those originally given.

In the previous paper it is said, "In many cases it is believed that the total amount of carbohydrates thus definitely determined in food materials, will be found to be appreciably less than the nitrogen-free extract estimated by difference." This discrepancy, amounting to twenty or thirty per cent., as based upon the earlier and erroneous starch determinations, is diminished by the later results, but still exists to an extent which cannot be overlooked, as will appear from the following summary:

RESPECTIVE PERCENTAGES OF DIFFERENT CARBOHYDRATES IN DIFFERENT FOOD STUFFS.

	Sucrose.	Invert sugar.	Dextrin.	Soluble starch	Normal starch	Pentosans.	Crude fiber.	Total.	Nitrogen-free extract.
Wheat I	0.52	0.08	0.27	0.00	57.62	4.54	2.68	65.71	77.07
Wheat II	0.72	0.00	0.41	0.00	56.27	4.37	2.51	64.28	77.66
Flour I	0.18	0.00	0.90	0.00	67.99	0.00	0.25	69.32	83.54
Flour II	0.20	0.00	1.06	0.00	67.76	0.00	0.25	69.27	84.54
Maize	0.27	0.00	0.32	0.00	65.45	5.14	1.99	73.17	78.02
Bread (Wheat I)	0.14	0.10	0.68	1.37	53.54	4.16	2.70	62.59	77.20
Bread (Wheat II)	0.05	0.32	0.23	2.36	53.62	4.34	2.42	63.34	77.33
Bread (Flour I)	0.06	0.37	0.27	1.99	64.81	0.00	0.34	67.84	82.94
Bread (Flour II)	0.15	0.38	0.91	1.74	64.12	0.00	0.17	67.47	85.17
Corn bread (Maize)	0.16	0.19	0.00	2.80	61.74	3.54	2.22	70.75	77.81

This discrepancy may arise from one of two sources; *viz.*, 1.

Error in the determination of carbohydrates. 2. The existence of a substance which is free of nitrogen and is of a character not usually ascribed to carbohydrates and resistant to the ordinary reactions for such. While the first alternative is not excluded, the writer is inclined to the latter conclusion and expects to continue the investigation along this line.

NOTE.

Improvement in Drying Chambers.—In an ordinary copper drying chamber, or air-bath, the bottom is protected by a false bottom, usually of iron, supported at the four corners by the legs of the chamber. When heated by a burner the false bottom expands and cups, and thus breaks the heat connection with the true bottom, making the chamber more difficult to heat. This trouble may be entirely remedied by riveting the two bottoms in the center with one rivet, leaving the four corners to expand or contract, but still supported by the legs of the chamber. The burner should be placed immediately under the rivet. The writer has used chambers thus improved for some time with great satisfaction. Chambers with the improved bottom may be had of Eimer & Amend, New York. J. L. BEESON.

NEW BOOKS.

THE ENERGY OF LIVING PROTOPLASM. By OSCAR LOEW. Professor in the Imperial University, Japan. 1896. London: Kegan Paul, Trench, Trübner & Co.

After reviewing briefly the theories of the cause of vital phenomena held from the time of Plato to the present, and after giving a short history of the discovery of the cell, the author takes up the characteristics of protoplasm, and especially those by which this substance exhibits phenomena of sensation. This naturally leads to a discussion of the relations of proteids to protoplasm, and consequently to a sharp distinction between physiologically active and dead or reserve proteid matter. He considers that proteids yield the vital phenomena, and that living proteid matter undergoes a chemical change at the moment of death. After briefly reviewing the older theories respecting the constitution of the proteid molecule he concludes with the following: "It appeared to me that more insight into the chemical nature of the proteids

could be obtained by the study of the *formation of proteids in plant cells*. Starting from a series of observations I reached a hypothesis which led me to infer the existences of a labile and stable modification of albumin, as explaining in a more satisfactory manner than the views of Pflüger and of Latham the difference between the proteids of living protoplasm and those of dead."

To get a clew to the formation of proteids he studied the nutrition of lower fungi and phaenogams. Microbes are especially characterized by their great chemical activity—one cell under favorable conditions multiplying in twenty-four hours to more than a trillion new cells. In this process the complex organic substances which serve as food are broken down, and by synthetic processes the protoplasm and other constituents of the plant cells are created. Although different chemical bodies serve as nourishment the same proteids are formed, for otherwise new species would result. He has found that the same species persists whether fed on glycerol, glucose, galactose, acetic or quinic acid; or whether leucin, betain, asparagin or kreatin furnish nitrogen.

From this it must be concluded that proteids are formed from substances so simple that they may be derived from each of these widely differing bodies. Since the simplest compounds which can be utilized by plants for the formation of proteids are methyl alcohol, methylamine, and methyl sulphuric acid, the "starting group must contain only one atom of carbon in the molecule."

"Since methyl alcohol and methylamine as such do not serve for synthetic operations, transformation into a compound capable of condensation must take place, and this can only be formaldehyde, the same substance that forms, by condensation, various kinds of sugars."

Formaldehyde is a poison, but owing to the extreme ease with which it is condensed, and to the fact that certain compounds of this aldehyde are quite harmless, this objection has no great weight, for no molecule remains unchanged for a second.

Bacillus methylicus, a species of microbe, can derive its entire organic nutriment from the acid sodium sulphite compound of formaldehyde as well as the compound of formaldehyde with ammonia. In the case of the nitrifying microbe, which can utilize ammonium carbonate, it is probable that formaldehyde

results from the carbon dioxide through the aid of the hydrogen of the ammonia.

By a similar line of reasoning Loew concludes that ammonia serves as the simplest source of nitrogen.

In regard to sulphur, there is little doubt that this is present in the proteid molecule in a reduced state and consequently sulphur compounds must be reduced to hydrogen sulphide in proteid formation. We may therefore infer that the atomic groups necessary for the formation of the proteid molecule are formaldehyde, ammonia, and hydrogen sulphide.

After discussing the relations of asparagin to proteid formation and decomposition, which has been so many times pointed out by numerous observers, he asks: "How can we explain the transformation of asparagin into albumin?" Asparagin, being a relatively simple compound, while albumin is one of the most complex, the latter must be derived from the former by some transformation which can readily take place. Such a process would be possible if aspartic aldehyde were formed and subsequently condensed.

The formation of albumin from formaldehyde and ammonia he represents as taking place according to this theory in the following way:

I. $$4CH_2O + NH_3 = \begin{matrix} COH & COH \\ | & | \\ CH_2 & CHNH_2 \end{matrix} + 2H_2O.$$

Aspartic aldehyde.

II. $$3C_4H_7N = C_{12}H_{17}N_3O_4 + 2H_2O.$$

Aspartic aldehyde. Intermediate product.

III. $$6C_{12}H_{17}N_3O_4 + 12H + H_2S = C_{72}H_{112}N_{18}SO_{22} + 2H_2O.$$

Lieberkühn's albumin formula.

For II it is assumed that condensation proceeds between the aldehyde and methylene groups, while in equation III condensation occurs after the type of pinacone formation, a highly unstable substance resulting, containing twelve aldehyde and eighteen amido groups, which possesses much kinetic energy in the form of motions of the labile atoms.

By atomic migration it would, with the loss of aldehyde characters, become a relatively stable substance, the ordinary albumin.

As evidence of the existence in the living cell of a peculiar active form of proteid, he describes an "active albumin" whose presence in a large number of plants was revealed by the action of dilute solutions of organic bases.

This form of albumin differs from passive albumin by a greater power of holding water in combination; by forming insoluble compounds with certain organic bases; by being coagulated with very dilute alcohol, ether vapor, and dilute prussic acid; and by reducing highly dilute silver solutions.

These differences from passive albumin are ascribed to the existence of active aldehyde groups in the molecule of the active albumin, which by atomic migration become converted into passive groups, as shown by the following formula:

Active. Passive.

The source of energy of living cells he ascribes to the kinetic energy of labile atoms within the proteid molecule and as evidence of this he compares the properties of living protoplasm with labile organic compounds, which are easily changed by heat, acids, or alkalies into stable, isomeric, or polymeric products, whereby contraction takes place and heat is developed. These labile bodies can cause chemical changes in other compounds, those containing labile hydrogen atoms having an especial affinity for oxygen.

Loew's theory of the formation of albumin supplies this necessary labile condition of protoplasm through the proximity of aldehyde and amido groups, for amido aldehydes have recently been shown to be very labile substances. As evidence of the existence of such groups in protoplasm the poisonous effect of substances readily reacting with aldehydes and amides is discussed at length. As aldehydes and amides react upon one another the danger of self-poisoning of protoplasm becomes great, a condition which the author considers as occurring when protoplasm is heated above 50°, its contained albumin being thereby changed from the active to the passive state in the manner indicated in the formula last given.

Coming next to a discussion of the chemical activity of the

living cell he finds the cause of this in the katalytic power of the protoplasm, which power is due to the oscillating motion of the labile atoms of the proteid constituents. It is by means of the energy imparted by these labile atoms that the oxidations occurring in respiration take place and thus this appears as the source of the energy of living protoplasm.

Whatever views the reader may hold respecting this theory and the evidence on which it rests he cannot fail to find much food for thought in the multitude of facts brought together in this volume. The book abounds in references so that a practically complete bibliography of the subject is given, a fact which alone gives the work much value.

THOMAS B. OSBORNE.

TABLES FOR THE DETERMINATION OF MINERALS BY PHYSICAL PROPERTIES, BASED ON THE SYSTEM OF DR. A. WEISBACH. By PERSIFOR FRAZER. Fourth Edition. pp. 163. Philadelphia: J. B. Lippincott Co. 1897. Price $1.50.

These tables are well printed, the arrangement clear, the various physical properties succinctly, yet accurately, enumerated, and the remarks on blowpipe reactions and associated minerals very well written. There is an unfortunate confusion in the use of the term "*sectile*," which as defined by Dana and used by accurate mineralogists, means that the substance can be sliced into shavings with a knife, but goes to pieces on hammering. Dr. Frazer uses *sectile* in place of Weisbach's *weich*, which is very clearly used as meaning simply *soft;* and again uses the same word in place of the German *mild*, which as used by Weisbach means that the substance is not brittle, but cuts like white china clay or stibnite. The result of this confusion is that the tables sometimes classify a mineral as sectile in one sense, but not sectile in another sense; while the same mineral is not sectile at all according to the definition of Dana!

It would have been far better to have used *soft* in the first case and *mild* in the second, explaining the meaning that word has when applied to minerals, while *sectile* could be reserved for its exact use according to definition.

Aside from these commendations and criticisms, and while acknowledging the tables the best of their kind, the reviewer must record his opinion that "*the kind*" is not the best one. Mineral

tables based on "physical properties" are radically wrong in principle. Dr. Frazer himself emphasizes in italics the truth that "*Every true mineral is a definite chemical compound or element*," and it thence follows that every true scheme of determining minerals should start and be based on their *chemical composition*, bringing in physical tests *afterwards* to verify the chemical determination, or to distinguish between the few minerals which contain the same ingredients or respond to the same tests. The Weisbach method starts at the wrong end, and while it may and does give to beginners a superficial acquaintance which enables them to identify the *usual* forms of the *common* minerals, yet it is totally unfit to guide in the accurate determination of minerals in general. JOSEPH W. RICHARDS.

PHYSICAL LABORATORY MANUAL FOR SECONDARY SCHOOLS. BY CHARLES F. ADAMS, A.M., Teacher of Physics in Detroit Central High School. 12 mo. pp. 184. 1896. New York and Chicago: Werner School Book Company. Price, 75 cents.

While the number of elementary manuals for physical laboratory instruction continues to increase, it is rare to observe among them any decided advance either in methods or plan. In the book before us the author has sought to eliminate qualitative exercises "or illustrative experiments," as he calls them, and to confine the pupil's attention to comparatively few exercises, the greater part of them being quantitative in character. It would seem, however, that, especially in elementary instruction, there is a proper place for qualitative physics as there certainly is for qualitative chemistry. Indeed, in certain parts of the subject, as, for instance, in physical optics and in electrostatics, qualitative experiments are an almost necessary preparation for quantitative ones. A judicious combination of the facts of physics, ascertained by qualitative experiments, with the laws of physics, proved and verified quantitatively, would seem to constitute the best basis for an elementary laboratory text-book. While there is not much that is novel in Mr. Adams' text-book it is well arranged, the experiments are for the most part well chosen, and the descriptions are clear and concise. The emphasis with which care in entering the results in the note-book is insisted on, is particularly to be commended. G. F. BARKER.

LABORATORY CALCULATIONS AND SPECIFIC GRAVITY TABLES. BY JOHN S. ADRIANCE, A.M. Third Edition. Revised and Enlarged. 1897. ix + 144 pp. Price, $1.25.

This little book, which is well known to many chemists, appears in a new and somewhat enlarged edition.

Many an analyst has felt impatient at the loss of time necessary in making analytical calculations. To such this book will be found useful, containing as it does calculations for most of the reagents employed in analytical chemistry. The percentage and specific gravity tables, which are numerous, as well as the directions for preparing many reagents, will be found convenient.

It is to be regretted that the atomic weights employed by the author could not have been taken from the recent edition of Professor Clarke's "Constants of Nature," instead of his tables published in 1882. The book as it is, however, will be useful to most chemists, and should find a place in every well regulated laboratory. J. F. MCGREGORY.

AN INTRODUCTORY COURSE OF QUANTITATIVE CHEMICAL ANALYSIS, WITH EXPLANATORY NOTES AND STOICHIOMETRICAL PROBLEMS. BY HENRY P. TALBOT, PH.D., Associate Professor of Analytical Chemistry in the Massachusetts Institute of Technology. 125 pp. New York: The Macmillan Co. Price $1.50.

There are few readers of analytical chemistry who have not felt the need of a book which shall in a clear and concise style give the principles of quantitative analysis, and sufficient of the practice to enable the student to make his way in the larger and fuller manuals. Such a book is needed not only for those who expect to become analytical chemists, but for the much larger number who pursue chemistry in colleges, merely in course of a general education. It is hardly too much to say that it is difficult to see how a better book could be prepared for this purpose than the one before us. The general directions and the specific directions under each analysis are so clearly given that an instructor could oversee the work of a large number of students, and in each case the theory of every step is so lucidly explained that the book has a distinct educational value. The examples are well chosen and illustrate the most important methods of procedure. They are in gravimetric analysis, chlorine, iron, sulphuric acid, phosphorus pentoxide, calcium and magnesium in dolomite, lead, copper (electrolytic), and zinc in

brass; in volumetric analysis, calibration, preparation of half-normal hydrochloric acid and sodium hydroxide, soda ash, oxalic acid, iron (bichromate), chromium in chrome iron ore, iron (permanganate), pyrolusite, iodimetry, antimony in stibnite, bleaching powder, and silver (potassium thiocyanate).

The book closes with a very useful chapter on stoichiometry, containing typical problems, and a table of four place logarithms. JAS. LEWIS HOWE.

TRAITÉ ÉLEMENTAIRE DE CHIMIE. PAR. A. HALLER, Correspondant de l'Institut, Directeur de l'Institut Chimique de la Faculté des Sciences de Nancy, et P. Th. Muller, Maitre de Conférences a l'Institut Chimique de la Faculté des Sciences de Nancy. Paris: Carré et Naud.

This work appears in two octavo volumes, the first of 336 pages, being devoted to inorganic chemistry, and the second, of 205 pages, to organic. It is a brief outline of general chemistry and presents nothing essentially new. Nevertheless, as an outline it is very complete, dealing with the entire subject in a clear and satisfactory manner, and including many topics which are usually discussed in larger text-books only. As an illustration of its scope it may be mentioned that attention is given to such subjects as argon, carborundum, and nickel carbonyl. In the volume upon organic chemistry the new nomenclature of carbon compounds is used, but this part of the work would be of greater interest to students if a systematic discussion of nomenclature were introduced. To American readers who wish to gain a knowledge of scientific French this work can be recommended. A chapter (19 pages) devoted to qualitative analysis will still further increase its value considered as a sort of introduction to French chemical literature. FRANCIS C. PHILLIPS.

NOTES ON ASSAYING. BY PIERRE DE PEYSTER RICKETTS, E.M., PH.D. AND EDMUND H. MILLER, A.M., PH.D. viii + 311 pp. New York: John Wiley & Sons. Price, $3.00.

The best part of this book is the part that does not treat of assaying; *viz.*, Parts III, IV, and V. These are devoted to chemical analyses, both quantitative and qualitative, blowpipe tests, laboratory extraction tests, and the usual tables, together with some new ones. Among the latter are tables of the characteristics of ores and of metals, and a table of solubilities. These features are good ones and make any laboratory handbook convenient and valuable.

Parts I and II, devoted to apparatus, reagents, and schemes for fire assays, contain so much useless and misleading information that the valuable portion is lost completely to the inexperienced reader. It would have been much better had the authors reduced these one hundred and thirty-nine pages to thirty.

HANDBOOK FOR THE BIO-CHEMICAL LABORATORY, INCLUDING METHODS OF PREPARATION AND NUMEROUS TESTS ARRANGED ALPHABETICALLY. BY JOHN A. MANDEL. New York: John Wiley & Sons. pp. 101. Price, $1.50.

In this little book the author presents a very good compilation of laboratory processes for the production of a number of substances of physiological importance. Many of the descriptions of methods appear to be taken from well-known books of Drechsel, Halliburton, Gamgee, and others, but a distinct service has been rendered American students by bringing them together in compact form. Most of the processes described have stood the test of student practice and can be recommended as workable.

A list of common tests, employed mostly in laboratories of physiological chemistry, takes up about thirty-five pages of the book. Some of these tests are good, others could have been omitted without lessening the value of the book, as they are practically useless in investigation. In this part of the book several typographical errors have escaped the notice of the author. On page 76, for instance, "liquor of potassæ" should not have been overlooked, and on page 85, under the Molisch test "solution of a naphthol" should read "solution of α-naphthol." Other errors noticed are of minor importance and not misleading. J. H. LONG.

BOOKS RECEIVED.

Tables for the Determination of Minerals by Physical Properties. By Persifor Frazer. xii + 163 pp. J. B. Lippincott Co. 1897. Price, $1.50.

The Wooly-Aphis of the Apple. Bulletin No. 35. Agricultural Experiment Station of the State of Missouri. Columbia, Missouri. July, 1896. 26 pp.

An Introductory Course of Qualitative Chemical Analysis with Explanatory Notes and Stoichiometrical Problems. By Henry P. Talbot, Ph.D. 125 pp. 1897. New York: The Macmillan Co. Price, $1.50.

Some Notes Concerning the Nitrogen Content of Soils and Humus. By Elton Fulmer. Bulletin 23. Washington State Agricultural College and School of Science. Pullman, Washington, October, 1896. 19 pp.

Experiments in the Culture of the Sugar Beet in Washington for 1895 and 1896. By Elton Fulmer. Bulletin 26. Washington State Agricultural College and School of Science. Olympia, Washington. December, 1896. 36 pp.

The Phase Rule. By W. D. Bancroft. 255 pp. Ithaca, N. Y.: Journal of Physical Chemistry. Price, $3.00.

The Chemistry of Dairying. By Harry Snyder, B.S. viii + 156 pp. Easton, Pa.: Chemical Publishing Co. 1897. Price, $1.50.

Studies in Chemical Dynamics. By J. H. van 't Hoff. vi + 286 pp. 1896. Easton, Pa.: Chemical Publishing Co. Price, $2.50.

Engineering Chemistry. By Thomas B. Stillman, M.Sc., Ph.D. With 154 illustrations. xxiv + 523 pp. Easton, Pa.: Chemical Publishing Co. 1897. Price, $4.50.

Principles and Practice of Agricultural Analysis. By H. W. Wiley, Chief Chemist U. S. Dept. of Agriculture. Vol. III. Agricultural Products. xii + 666 pp. Easton, Pa.: Chemical Publishing Co. 1897. Price, $3.75.

Corn, Cotton, and Forage Plants. Bulletin No. 40. Texas Agricultural College, College Station, Brazos Co., Texas. September, 1896. 24 pp.

A Clinical Report on the Chemical Examination of Two Hundred Cases of Human Breast Milk. By Vanderpoel Adriance, M.D., and John S. Adriance, A.M., F.C.S. 42 pp.

Thirty-Fourth Annual Report of the Massachusetts Agricultural College. Public Document No. 31. January, 1897. 356 pp. Boston: Wright & Potter Printing Co. 1897.

Experiments with Corn and Crimson Clover, and Growing Cattle Without Coarse Feed. Bulletin No. 46. January, 1897. 24 pp. University of Illinois, Agricultural Experiment Station, Urbana, Ill.

Dairy and Food Laws of Wisconsin for the Years 1895–1896. H. C. Adams, Commissioner. 315 pp. Madison, Wisconsin. Democrat Printing Company, State Printers.

Digest of Criticisms on the United States Pharmacopœia, Seventh Decennial Revision (1890). Part I, comprising abstracts of paper to July 1, 1896. 183 pp. Published by The Committee of Revision and Publication of the Pharmacopœia of the United States of America (1890–1900).

The paper on "The Distribution of the Precious Metals in Copper," by Edward Keller, printed in the March issue of this Journal, was presented at the February meeting of the American Institute of Mining Engineers. Mention of this fact should have been made.